Novel Phenothiazine-Derived Organic Dyes for Visible-Light-Driven Dye-Sensitized Photocatalytic Hydrogen Production

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Production of hydrogen is key for establishing clean energy systems, because it can be used as a clean energy source in fuel cells [1]. Although some semiconductors have decent visible-light-driven photocatalytic activity, many challenges still remain. Such challenges include improving the water splitting efficiency and stability of catalysts through the engineering of the semiconductor [2]. Another approach for visible-light-driven photocatalytic water splitting for hydrogen production is a dye-sensitized photocatalytic water splitting system. A Ru-complex dye has high efficiency for dye-sensitized photocatalytic water splitting. Compared to metallic materials, metal-free organic dyes have the advantage of being environmentally friendly, abundant, cheap, and flexible. Furthermore, it can be easy modify of the energy gap by modifying of the organic materials structure. In this study, we investigated visible-light-driven photocatalytic activity in a novel donor–spacer–acceptor dye on TiO_2/Pt system.

The title material of dyes were synthesized for this experiment. When the spacer parts were inserted between donor and acceptor as bridge units, the absorption maxima of bathochromic shifted were showed. Competition in the hydrogen production performances between dyes **2** and **3** is worth mentioning. The dye of **2** produced 322 μmol of hydrogen gas after 14 h and **3** produced 679 μmol. Based on the results, the turnover number (TON) and frequency (TOF) after 14 h were better for dye **3** (TON: 1414, TOF: 101) than for dye **2** (TON: 708, TOF: 51). The hydrogen production performance of dye **1** was very low (TON: 22, TOF: 1.6) after 14 h. To investigation of these reason, we have measured the time-dependant absorption spectra of dyes on TiO_2. Clearly, the time profiles for **1**–**3** indicate that the lifetime of radical cation species (τ_1 ad τ_2) could increase as the number of spacers between the donor and acceptor increases. This fact suggests that the spacer effect could extend the charge recombination lifetime and electron injection lifetime between the dye and TiO_2, because the time for an electron to return to the dye or donor site from TiO_2 could be enhanced by separation with spacers.

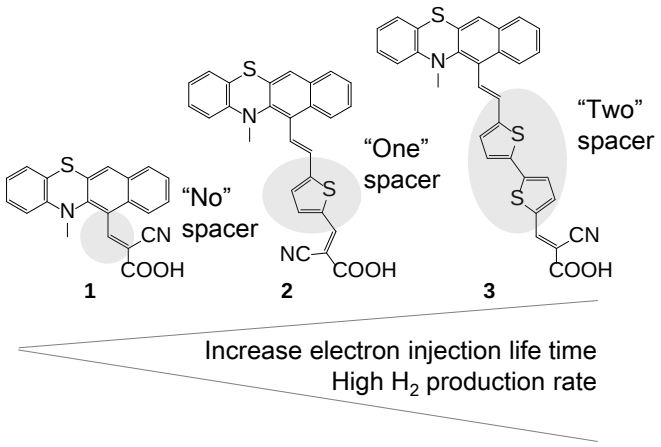

Fig. 1. The model dyes **1**–**3** in this study.

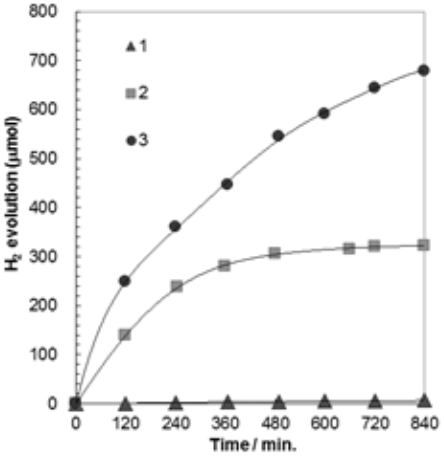

Fig. 2. Photocatalytic activities of the dyes **1**–**3** for water splitting reactions. Reaction conditions: 10 mL of 10 vol% TEOA aq., 33.0 mg dye–TiO_2–Pt catalyst, pH = 7.0. A 300 W Xe lamp was used (the light below 420 nm was cut off by an optical filter).

References

[1] a) C. Song, *Cat. Today*, 2006, 115, 2. b) T. E. Mallouk, *Nat. Chem.*, 2013, 5, 362. [2] A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, 38, 253.