

Visible-light-induced vectorial electron transfer at Ru(bpy)₃ intercalated alternately stacked titanate nanosheets and tungstate nanosheets.

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Layered nanostructures composed of metal oxide nanosheets are promising materials for a solar energy conversion system, since these nanostructures have hetero interfaces with large area. Recently, we reported a one-step synthesis method for an alternating stacked structure by thiol-ene click reaction of thiol-grafted titanate nanosheets and alkene-grafted tungsten nanosheets^[1]. Cationic species can be intercalated into the interlayer space of the nanostructure. Since almost all the cationic molecules can be orderly aligned with the nanosheets, electron transfer reactions between the stacked nanosheets and the intercalated molecules proceed efficiently^[2].

In this study, we demonstrate visible-light-induced Z-scheme vectorial electron transfer reactions at the Ru(bpy)₃ intercalated alternate stacked nanostructure, which is synthesized by thiol-ene click reaction of titanate nanosheets modified with Pt(terpy) at the edge and tungstate nanosheets (Fig. 1).

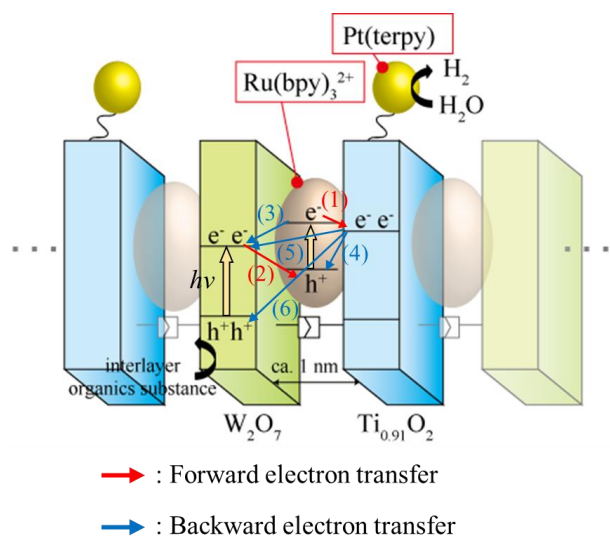


Fig. 1 The expected electron transfer in the alternate stacked structure.

From the fluorescence decay of intercalated Ru(bpy)₃ as shown in Fig. 2(a), the rate constant of the forward electron transfer reaction (1) is estimated at $1.16 \times 10^8 \text{ s}^{-1}$, while the backward electron transfer reaction (3) is estimated at $1.02 \times 10^7 \text{ s}^{-1}$. Fig. 2(b) shows that the electrons in conduction band of tungstate generated by 370 nm monochromatic light irradiation are consumed by photoexcitation of Ru(bpy)₃ under 500 nm light irradiation, demonstrating the forward electron transfer (2). From this result, we can conclude that the electron transfer (2) is faster than the backward electron transfer (4).

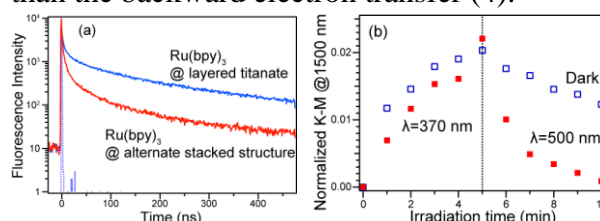


Fig. 2 (a) Fluorescence decay of intercalated Ru(bpy)₃. (b) Quantification of the conduction band electrons in tungstate.

From our previous report^[3], the rate of backward electron transfer reaction (5) was exponentially decreased with the increase of stacking distance. In the current study, the stacking distance of nanosheets is determined as 2.32 nm by X-ray diffraction, where the electron transfer rate is expected to be zero.

Consequently, the forward electron transfer reactions proceed preferentially as the competition of the process of (1)-(6). The electrons getting to the conduction band of the titanate can reduce water to dihydrogen, where the Pt(terpy) plays a role as co-catalyst (Fig. 3).

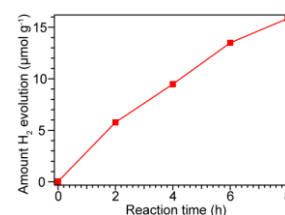


Fig. 3 Amount of dihydrogen evolution under visible light irradiation ($\lambda > 420 \text{ nm}$).

REFERENCES

- [1] D. Mochizuki, K. Kumagai, M. M. Maitani and Y. Wada, *Angew. Chem. Int. Ed.*, 51 (2012) 5452.
- [2] F. Kishimoto, D. Mochizuki, K. Kumagai, M. M. Maitani, E. Suzuki and Y. Wada, *Phys. Chem. Chem. Phys.*, 16 (2014) 872.
- [3] D. Mochizuki, K. Kumagai, M. M. Maitani, E. Suzuki and Y. Wada, *J. Phys. Chem. C*, 118 (2014) 22968.