Artificial imitation of one-way electron transfer in natural photosynthesis system by hetero-stacked nanostructure of titanate and tungstate nanosheets position-selectively modified with Pt(terpy) and $Ru(bpy)_3$

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Abstract: In an artificial photosynthesis system, a suppression of backward electron transfer reaction to make photoinduced electron transfer processes 'one-way' is a crucial issue to improve its efficiency. We constructed a precisely designed hetero-stacked structure of titanate nanosheets and tungstate nanosheets modified with $Ru(bpy)_3$ and Pt(terpy). In the structure, Pt(terpy) modified at the edge of the titanate nanosheets can reduce water by using the electrons in the conduction band of titanate, which is transferred from the conduction band of tungstate via photoexcited $Ru(bpy)_3$. The backward electron transfer reactions in the structure can be successfully suppressed by the angstrom-ordered placement of the titanate nanosheets, the tungstate nanosheets and the intercalated $Ru(bpy)_3$.

Keywords: Artificial photosynthesis, Heterojunction, Nanostructure catalysts.

1. Introduction

Solar energy conversion systems are promising devices for reducing our dependence on fossil fuels. In particular, artificial photosynthesis systems for a hydrogen production are widely researched. The targeted solar-to-hydrogen conversion efficiency for such an artificial photosynthesis system is 10 %. However at the present moment, the conversion efficiency was reached to 1.1 % at highest[1]. Therefore, new concepts to drastically increase the efficiency are much needed.

In the general artificial photosynthesis systems, the powder of two types of semiconductors are dispersed in a medium, and the electron transfer reaction between the oxygen evolution photocatalysts to the hydrogen evolution photocatalysts is mediated by the dissolved redox couples (Fig. 1(a)). In such a conventional system, the backward electron transfer reaction from the hydrogen evolution photocatalyst to the oxygen evolution photocatalyst is also mediated by the dissolved redox couples. The efficiency of these systems is a consequence of the balance of forward and backward electron transfer reactions. Therefore, the suppression of backward electron transfer reaction to make the electron transfer reaction system 'one-way' is the most important issue.

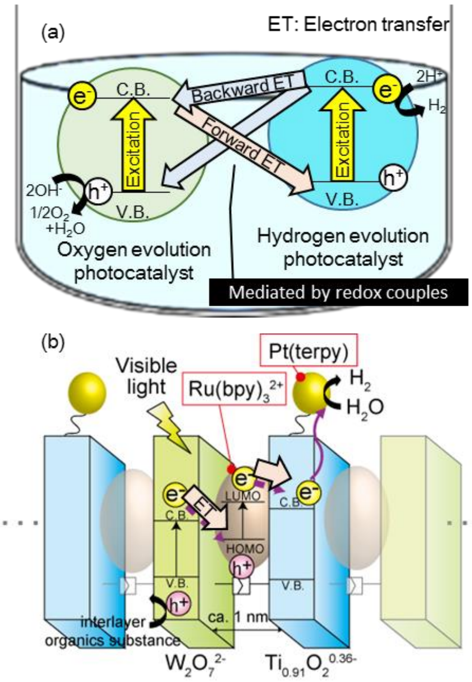

Figure 1 (a) Conventional artificial photosynthesis system, and (b) proposed artificial photosynthesis by using stacked nanosheets.

In the current study, we proposed that a dye-intercalated alternate-stacked structure (Fig. 1(b)), made from thiol-functionalized titanate nanosheets ($Ti_{0.91}O_2^{0.36-}$) and alkene-functionalized tungstate nanosheets ($W_2O_7^{2-}$) via a thiol-ene click reaction[2], provides a precisely controlled construction that allows one to understand and control the overall forward and backward electron transfer reactions.

2. Experimental

Pt(terpy)Cl was immobilized at the edge of titanate nanosheets in layered structure ($H_{0.36}Ti_{0.91}O_2$) through an amino-function silane coupling reagent via a dehydrochlorination reaction. After the interlayer space of layered titanate was expanded by an intercalation of n-octylamine, the face of each layers of titanate was modified with a thiol-function silane coupling reagent. The exfoliated thiol-functionalized titanate nanosheets and alkene-functionalized tungstate nanosheets were alternately stacked via thiol-ene click reaction. $Ru(bpy)_3^{2+}$ was introduced into the interlayer space by ion-exchange with the n-octylammonium cation in interlayer space.

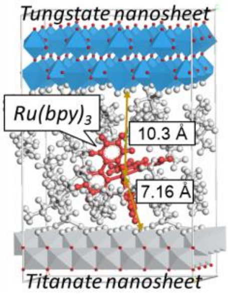

Figure 2 Simulated structure of intercalated molecules calculated by a molecular dynamics method for 50ps.

3. Results and discussion

To evaluate the photoinduced electron transfer reactions in the alternate stacked structure, the fine structure should be recognized. The most stable structure of the interlayer molecules were simulated by a molecular dynamics (MD) method using the Forcite module in Materials studio 2017 R2. Before the MD method, the geometry of interlayer molecules was optimized by DFT method with a condition that the position of the $Ru(bpy)_3^{2+}$ was fixed at the center of the interlayer space. Then the dynamics of the intercalated molecules were simulated for 50 ps where the $Ru(bpy)_3$ can flow freely. Consequently, we can conclude that the $Ru(bpy)_3^{2+}$ should be localized at the vicinity of the titanate nanosheets in the steady state (Fig. 2). The localization can be explained by an stronger electrostatic attractive force between the negatively charged titanate nanosheets and $Ru(bpy)_3^{2+}$ than that between the tungstate and $Ru(bpy)_3^{2+}$.

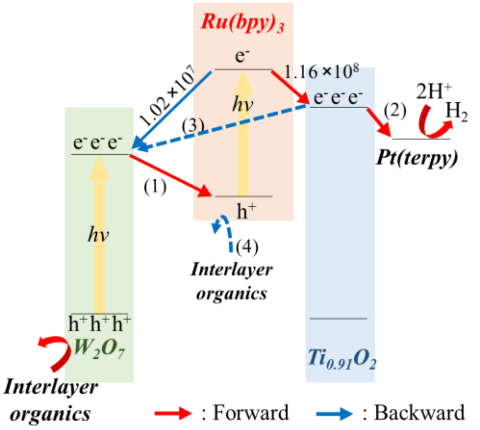

Figure 3 Overall forward and backward electron transfer reactions in the $Ru(bpy)_3^{2+}$ intercalated alternate-stacked structure of Pt(terpy) immobilized titanate and tungstate.

The dynamics of photoinduced electron transfer reactions from $Ru(bpy)_3$ can be estimated from a fluorescence decay of the intercalated $Ru(bpy)_3$. Due to the localization of $Ru(bpy)_3$ close to titanate nanosheets, the rate of a forward electron transfer from the LUMO level of photoexcited $Ru(bpy)_3$ to the conduction band of titanate ($1.16\times10^8 s^{-1}$) was 10 times faster than that of a backward to the conduction band of tungstate ($1.02\times10^7 s^{-1}$). The forward electron transfer denoted as (1) was demonstrated by the transitional quantitative measurement of the electrons in the conduction band of tungstate by the near-infrared absorption spectroscopy. From our previous report[3], the rate of backward electron transfer from the conduction band of titanate to that of tungstate, denoted as (3), 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 electrons getting to the conduction band of the titanate can reduce water to dihydrogen, where the Pt(terpy) plays a role as co-catalyst.

4. Conclusions

The localization of $Ru(bpy)_3$ close to the titanate nanosheets makes the forward electron transfer from the $Ru(bpy)_3$ to the titanate faster than the backward from the $Ru(bpy)_3$ to the tungstate. The backward from the titanate to the tungstate was suppressed by the enough distance of these nanosheets. Consequently, the electrons can reduce water to dihydrogen on the Pt(terpy) immobilized at the edge of the titanate nanosheets.

References

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