Biphasic Z-Scheme Photocatalytic System Using a Phase-Migrating Electron Mediator

Ren ITAGAKI[1,2], Akinobu Nakada[1*], Hajime Suzuki[1], Osamu Tomita[1], Ryu Abe[1*]
[1]*Kyoto University, Grad. Sch. of Eng., Kyoto daigaku-katsura, Nishikyo-ku, Kyoto, Japan.*
[2]*JSPS Research Fellow DC1, Kojimachi Business Center Building, 5-3-1 Kojimachi, Chiyoda-ku, Tokyo, Japan.*
** nakada@scl.kyoto-u.ac.jp (A.N.), ryu-abe@scl.kyoto-u.ac.jp (R.A.)*

Significance and Relevance

In recent years, photochemical molecular conversion reactions giving value added product have been attracting attention. Ideally, water should be used as an electron source to drive reductive photocatalytic reaction which only proceeds in organic solvent. In this study, we demonstrated a reductive photoredox catalysis coupled with water oxidation by separating the redox reaction fields with immiscible water/1,2-dichloroethane solutions and a ferrocenium/ferrocene phase-migrating electron mediator.

Preferred and 2nd choice for the topic: “Fundamental advances in understanding catalysis” or “Photocatalysis and photoelectrocatalytic approaches, solar energy utilization”…………………….
Preferred presentation: Poster………….

Introduction and Motivations

An artificial Z-scheme reaction system composed of two different photocatalysts[1] is a potential strategy for linking water oxidation with various reduction-based molecular transformations. We have developed a stepwise Z-scheme photocatalytic system using a biphasic solution using organic solvent that is immiscible with water.

Materials and Methods

The photocatalytic reductive coupling of benzyl bromide (Bn-Br) was performed by visible light irradiation of a biphasic solution of 1,2-dichloroethane (DCE) containing ferrocene (Fc; 5 or 10 mM), a photoredox catalyst (Ir-photosensitizer; 0.05 mM) and Bn-Br (50 mM) and H_2O exposure to visible-light ($\lambda > 400$ nm) under Ar atmosphere. The photocatalytic water oxidation was carried out in a suspension of a semiconductor photocatalyst (Bi-based oxyhalide) in an aqueous Fc^+ solution exposure to visible-light ($\lambda = 430$ nm) under Ar atmosphere. The evolved gases were analyzed by a O_2 sensor and the products in a liquid phase were analyzed by UV-vis absorption spectroscopy and HPLC.

Results and Discussion

Visible-light irradiation to a biphasic solution that composed of water and DCE solution containing a photoredox catalyst, Fc, and Bn-Br facilitated the reductive coupling of Bn-Br to dibenzyl (Bn_2; Figure 1a). Importantly, Fc^+, generated by photooxidation, migrates to the aqueous phase due to the drastic change in its partition coefficient compared to that of Fc.[2] On the other hand, visible-light irradiation to the same solution without water phase failed to generate any product (Figure 1b). This finding indicates that the phase migration of Fc^+ across a biphasic solution suppresses the unfavorable backward charge recombination, which enables the photoreduction of Bn-Br (Figure 1b).

The results on the coupled phase migration/photoinduced electron transfer prompted us to further investigate design principles in order to improve the efficiency of this photocatalytic reaction. The co-existence of anions can further modify the driving force of phase migration of Fc^+ depending on their hydrophilicity; the best photocatalytic activity was obtained with 100% yield for prepared Fc after continuous photocatalysis for 90 min in the presence of $NBu_4^+Br^-$ (red plots in Figure 1c). Thus, the liquid-liquid phase migration of the mediator results in effective charge separation, which leads to facilitate the reduction of Bn-Br in the DCE phase.[3]

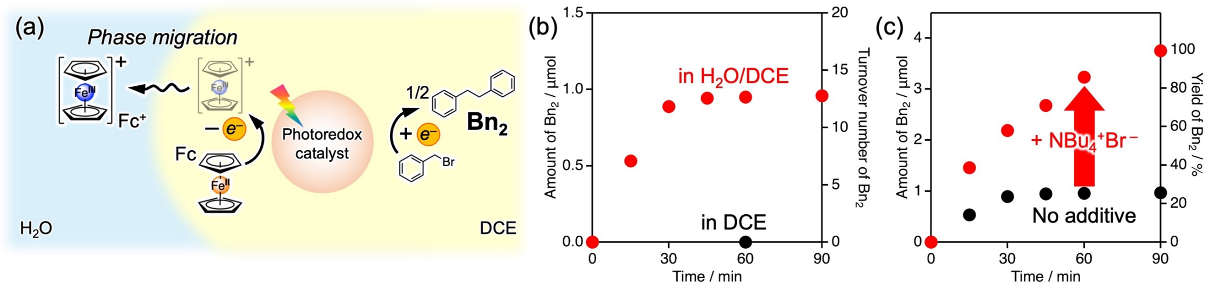


Figure 1 (a) Biphasic photocatalytic system for reductive coupling of Bn-Br designed in this study, time course of Bn_2 generation (b) in the DCE solution in the absence and presence of aqueous phase, and (c) in a H_2O/DCE (1:1, *v*/*v*) biphasic solution without additive (black plots) and in the presence of $NBu_4^+Br^-$ (red plots) under exposure to visible-light ($\lambda > 400$ nm).

On the other side, photogenerated Fc^+ can be utilized as an electron acceptor for photocatalytic water oxidation with a semiconductor photocatalyst in the aqueous phase (Figure 2b). In an aqueous solution, a semiconductor photocatalyst performed photocatalytic water oxidation with a Fc^+ electron acceptor which was generated after photocatalytic reduction of Bn-Br using Fc explained above, generating O_2 and Fc (Figure 2b). More importantly, the ratio of generated Bn_2 (5.0 µmol) and O_2 (2.5 µmol) satisfies the stoichiometry corresponding to the overall reaction (Figure 2b and c; Eq. 1).

Eventually, the Fc^+/Fc redox couple transports an electron by the photoredox induced liquid-liquid phase migration to achieve photoreduction of Bn-Br coupled with water oxidation (Eq. 1).

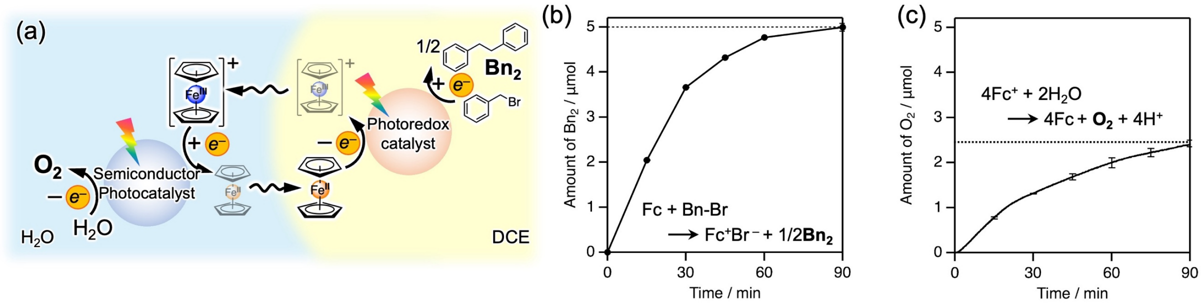
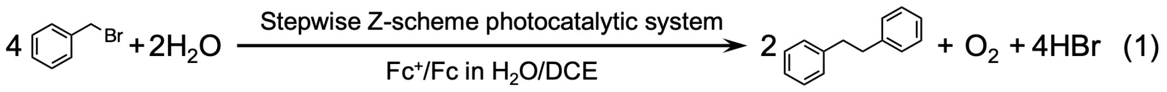


Figure 2 (a) Conceptual scheme of a biphasic Z-scheme photocatalytic system using Fc^+/Fc as a phase-migrating electron mediator. Time course of half reactions of (b) Bn_2 formation using photoredox catalyst and Fc as an electron donor in a H_2O/DCE (1:1, *v*/*v*) biphasic solution under exposure to visible-light ($\lambda = 470$ nm), and (b) O_2 evolution using photogenerated Fc^+ by Bn_2 production as an electron acceptor and a semiconductor photocatalyst under exposure to visible-light ($\lambda = 430$ nm) by a stepwise one. The dashed line shows the upper limit of Bn_2 and O_2 evolution expected from the amount of Fc added to these solutions.



References

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