Development of function-Integrated catalytic system for small molecule conversion

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Abstract

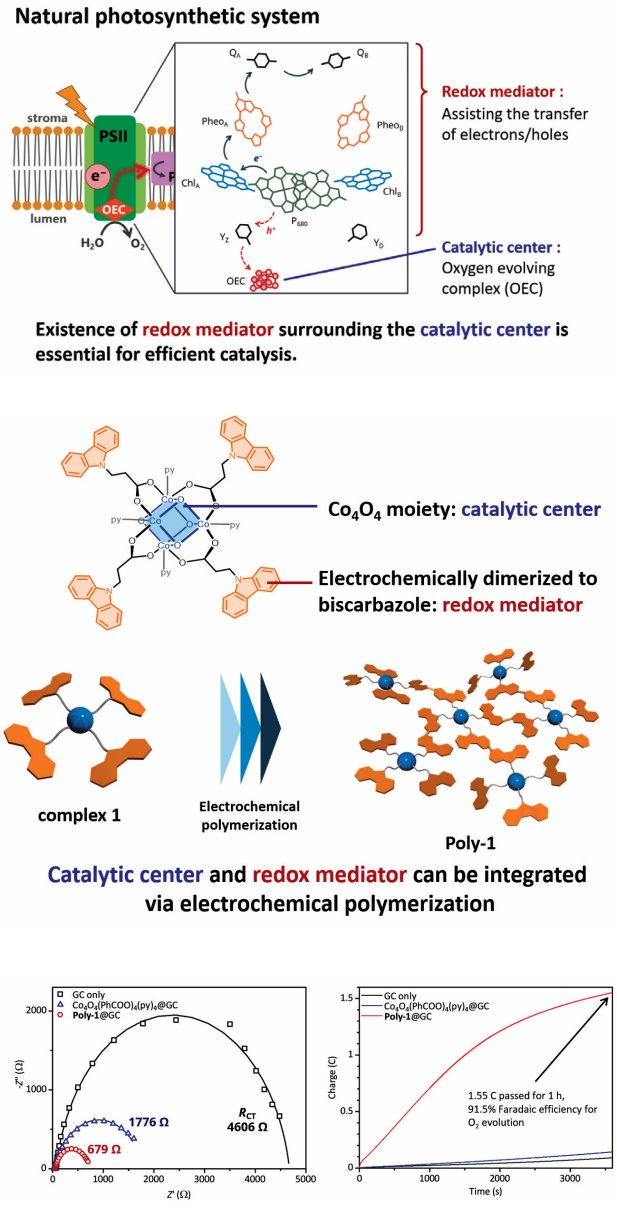
Four-electron oxidation of water ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is an important reaction for suppling the protons and electrons required to generate reduced products (i.e., chemical energy) from abundant resources in a clean manner. In this study, inspired by the natural water oxidation system, we hypothesized that the integration of catalytic centers and hole transporters into one material could be a promising strategy for obtaining efficient catalytic system for water oxidation. Based on this strategy, a polymer-based catalytic system (**Poly-1**) was constructed by assembling catalytic center and hole transporter units. **Poly-1** exhibited high hole transporting ability, and can promote water oxidation with a high faradaic efficiency and a low overpotential. This performance of **Poly-1** is of the highest class compared to the relevant systems.

Background & Results

Demand for a sustainable society and clean energy production has increased in recent years. In this context, the construction of catalytic system for artificial photosynthesis has attracted considerable attention. Water oxidation is regarded as a key reaction in artificial photosynthesis, and the efficient catalyst for the reaction is highly required. In this study, a novel approach for developing an artificial catalytic system for water oxidation was demonstrated. Inspired by the natural photosynthesis, we constructed an artificial water oxidation system that have a catalytic center surrounded by hole transporting units. A metal-complex-based precursor composed of a tetranuclear cobalt moiety as a catalytic center and carbazole ligands, was newly designed and synthesized. By the electrochemical polymerization of the complex, carbazole moieties of the complex dimerized to form biscarbazole moieties, which can act as hole transporter, and the polymer-based material (**Poly-1**) was successfully obtained. Electrochemical impedance spectra of **Poly-1** and the cobalt cubane complex without biscarbazole moieties revealed that charge transfer ability is largely enhanced due to the biscarbazole moieties embedded in **Poly-1**. Controlled potential electrolysis of **Poly-1** resulted in the evolution O_2 as confirmed. The performance of our catalytic system (the overpotential (η = 413 mV) and Faradaic efficiency (91.5%)) was found to be of the best class compared to the relevant Co complex-based catalytic systems. Note that the catalytic activity is almost suppressed when the complex without biscarbazole moieties was used as a catalyst. These results clearly demonstrate that the integration of two functions into one material is a key to develop the efficient water oxidation system.

Significance of the research and Future perspective

In nature, the water oxidation is efficiently catalyzed by a metal-complex-based catalyst (the oxygen-evolving complex, OEC) surrounded by hole-transporting amino acid residues. However, in artificial systems, there is no example of the water oxidation system which has a catalytic center surrounded by hole transporters. Our study is a significant example of a molecule-based catalytic system that mimics the key features of the OEC. Collectively, the present study offers a novel concept for obtaining efficient catalytic system for water oxidation.



Patent

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