A Highly Stable Molecular-based TiO₂ Photoanode for Photoelectrochemical Water Splitting Achieved by Pyridyl Anchoring Technique

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Recently, overall water splitting by a molecular-based photoelectrochemical cell has attracted considerable attention because it is regarded as one of the promising methods for solar-to-hydrogen conversion. In this context, extensive efforts have been thus far devoted to develop a highly efficient and stable molecular-based photoanode for water oxidation by modification of semiconductors with both a photosensitizer and a water oxidation catalyst (WOC). However, the poor stability of the molecular-based photoanodes in aqueous media due to the detachment of such functional molecules from the semiconductor surfaces is still one of the most serious problems to achieve such photoanodes. On the other hand, we previously demonstrated that the mesoporous TiO₂ electrode modified with Ru-qpy photosensitizer can act as a highly stable and efficient photoanode for solar driven hydrogen production in the presence of sacrificial electron donor (EDTA) since the chemisorption of Ru-qpy by pyridyl anchors is highly stable even in aqueous media.^[1]

In this study, Ru(bda)-py $WOC^{[2]}$ is incorporated to the Ru-qpy-modified TiO_2 electrode to develop a highly stable molecular-based photoanode because this WOC is expected to strongly chemisorb to the TiO_2 surfaces by using one of the two pyridyl rings. The molecular-based photoanodes were prepared by the stepwise adsorption of Ru-qpy and Ru(bda)-py in this order, and the amounts of adsorbed



molecules were estimated to be 0.16 and 0.02 μ mol/cm², respectively. This photoanode generates the steady anodic photocurrent density about 90 μ A/cm² under intermittent visible light irradiation in an acetate buffer (pH 5.0), strongly suggesting that photoelectrochemical water oxidation promotes at the surfaces of the photoanode. As expected, O₂ production is confirmed to proceed with over 90% Faradaic efficiency by the controlled potential electrolysis (CPE) under continuous irradiation when the electrode potential is held at 0.05 V vs. SCE. More importantly, the catalytic performance of this photoanode can be effectively improved by the pyridyl anchoring technique invented by our group. It is further confirmed that overall water splitting also proceeds with over 90% Faradaic efficiency for both O₂ and H₂ production when a small electrical bias (0.4 V vs. cathode) is applied, and relatively large solar-to-hydrogen conversion efficiency (0.07%) is obtained in our molecular-based photoelectrochemical cell.

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