Photoelectrochemical Conversion of Toluene to Methylcyclohexane as an Organic Hydride by Cu₂ZnSnS₄-Based Photoelectrode Assemblies

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ABSTRACT: Direct photoelectrochemical conversion of toluene (TL) to methylcyclohexane (MC) with water has been examined as an organic hydride conversion using light irradiation. The production of MC from TL was observed on Pt/CdS/Cu₂ZnSnS₄/Mo photoelectrodes with anion-type ionomer membrane assemblies. A cathodic photocurrent was observed below 0.7 V vs RHE (V_{RHE}) in 0.1 M Na₂SO₄/NaOH (pH 9.5) aqueous solution, and an apparent photocurrent density of 0.5 mA cm⁻² was obtained at 0 V_{RHE} under the irradiation of a 300 W Xe lamp with a 420 nm cutoff filter. The yield of MC was measured by gas chromatography, and an 88% faradaic efficiency was estimated. This study suggests the possibility of direct energy conversion from solar energy to MC as an energy carrier of organic hydrides.

Solar energy conversion to chemical energy is an attractive technology for realizing a renewable energy society. Various attempts to produce hydrogen by water splitting using photoelectrochemical (PEC) systems have been carried out.[1−4] Hydrogen is regarded as a central chemical energy carrier as a renewable energy source because of the large variety of hydrogen sources available and the wide range of potential uses. However, one of the inadequacies of hydrogen is its low energy density, which requires that high pressures or cryogenic temperatures be used for its storage and transportation. Organic hydrides are expected to be efficient carriers of hydrogen since they are usually liquid at ambient temperature and pressure.[5] Therefore, the present infrastructure for liquid fuels such as industrial tanks and oil tankers can be utilized for organic hydrides with small refinement. Benzene and toluene (TL) can be easily converted to cyclohexane and methylcyclohexane (MC), respectively, by an additional reaction with H₂ using a metal catalyst such as Pt, and conversely, cyclohexane and MC release H₂ under mild conditions using similar catalysts.[5] Organic hydrides are not only expected to be used to discharge H₂ but are also anticipated to be used as fuels in direct organic hydride fuel cells.[6] Because of the lower toxicity of TL relative to benzene and the similarity of their properties to those of conventional liquid fuels, TL/MC is one of the most promising systems for hydrogen storage. The direct synthesis of MC from TL and water using solar radiation has enormous significance in terms of the simplicity of the process

as well as reduced energy losses in comparison with multistep processes. The thermodynamic chemical reaction for the conversion of TL to MC with water is shown in eq 1, where

$$\text{(TL)} + 3\,H_2O = \text{(MC)} + 1.5\,O_2 \quad \Delta_r G^0 = -618\ \text{kJ mol}^{-1} \tag{1}$$
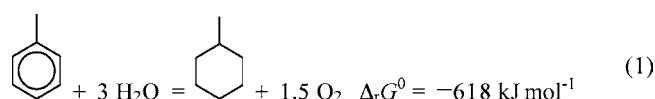
the standard reaction Gibbs free energy, $\Delta_r G°$, was estimated from standard formation enthalpies, $\Delta_f H°$, and standard molar entropies, $S°$, in the database.[7] This reaction free energy corresponds to 1.07 V on the basis of a six-electron reaction, and this value indicates that the electrochemical conversion of TL to MC with water is energetically easier than water splitting (1.23 V). In this work, we approached the direct conversion of TL to MC with water using light energy by means of a double-phase photoelectrochemical cell equipped with a photocathode assembled with an ionomer membrane.

Copper-based chalcogenides are promising photovoltaic materials, and their application to photoelectrochemical hydrogen evolution has attracted significant attention.[8−15] In this class of materials, Cu₂ZnSnS₄ (CZTS) has a direct band gap of 1.5 eV and comprises only naturally abundant elements. CZTS can be obtained by the sulfurization of electrochemically deposited layers of metal precursors using H₂S, which allows it to be prepared on substrates with complicated shapes.[13] CZTS photoelectrodes behave as p-type semiconductors and show photocathodic currents. The onset potential for a CZTS photoelectrode with appropriate surface modifications for hydrogen evolution from water electrolysis is ca. 0.7 V vs RHE (V_{RHE}; RHE = reversible hydrogen electrode),[12] indicating that CZTS has the potential for energy conversion from light to hydrogen. For example, modification with CdS, which is an n-type semiconductor, increases the onset potential and enhances the photocurrent because a p−n junction structure forms on the outmost layer and enhances the charge separation of the photogenerated carriers.[12−15] Pt particles on the surface are needed to catalyze hydrogen evolution. To apply a photoelectrochemical method to the conversion of TL to MC, a key issue is the formation of a reaction field wherein the hydrophobic TL is in contact with water and the photo-

electrode. To meet this requirement, a newly designed ionomer-membrane/photoelectrode assembly with three-phase interfaces was designed using CZTS. The photoelectrode was fabricated on a Mo mesh substrate to ensure smooth ion transfer.

In this paper, we report a photoelectrochemical system for the direct conversion of TL to MC with water using CZTS-based photocathodes. The high faradaic efficiency of this system suggests the possibility of producing MC from TL using solar irradiation. Direct PEC energy conversion to an organic hydride has not been reported previously, and the potential of this system for such a conversion is discussed.

A CZTS layer was fabricated by electrochemical deposition of Cu, Sn, and Zn on a Mo mesh substrate followed by sulfurization in an H_2S flow at 823 K for 1 h. The obtained CZTS layer was covered with CdS by chemical bath deposition (<100 nm thickness), and the outer layer was finally modified with Pt particles by photoelectrodeposition to catalyze the TL/MC reaction.[5,6] To fabricate the ionomer/photoelectrode assembly, the Pt/CdS/CZTS/Mo mesh photoelectrode was hot-pressed on an anion ionomer sheet (Tokuyama AHA) and then wetted with ionomer dispersion droplets. A schematic drawing of the ionomer/photoelectrode assembly is shown in Figure 1A. The detailed conditions used for the photoelectrode
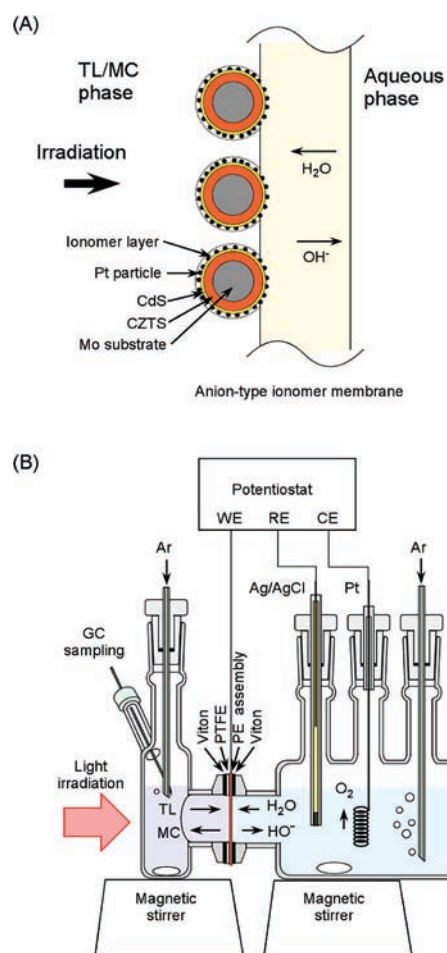

Figure 1. Schematic drawings of (A) the ionomer/photoelectrode (PE) assembly and (B) the PEC cell.

preparation are described in our former research.[13] The photoelectrode assembly was mounted in a two-phase PEC

cell, as shown in Figure 1B. The potential of the photoelectrode [the working electrode (WE)] was controlled by a potentiostat against an Ag/AgCl reference electrode (RE), which was calibrated against the RHE, and a Pt counter electrode (CE). The current density was derived from the current using the area of the assembly (10 mm diameter) and the aperture ratio of 62% (apparent electrode area of 0.30 cm^2). The aqueous chamber of the cell was filled with 100 mL of 0.1 M Na_2SO_4/NaOH (pH 9.5), and the organic chamber was filled with 4 mL of pure TL. The ratio of MC with respect to TL in the organic chamber was analyzed by gas chromatography (GC).

Scanning electron microscopy (SEM) images of the Pt/CdS/CZTS/Mo photoelectrode without and with the ionomer are shown in Figure 2. The image of the Pt/CdS/CZTS/Mo
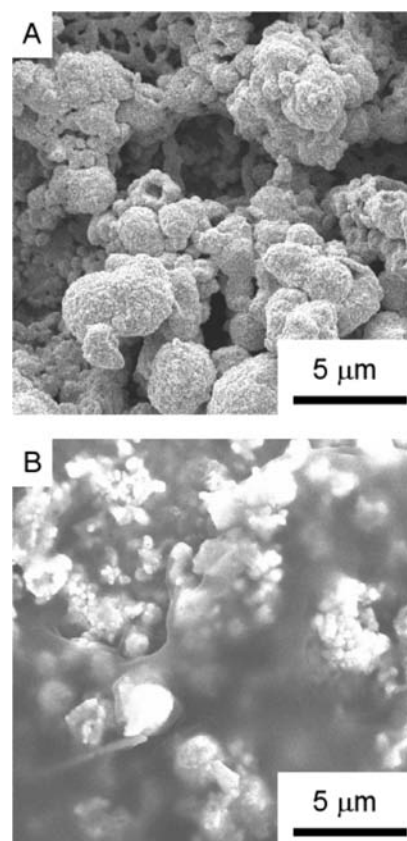
Figure 2. SEM images of (A) a bare Pt/CdS/CZTS/Mo photoelectrode and (B) a Pt/CdS/CZTS/Mo photoelectrode assembled with an anion ionomer membrane using ionomer dispersion.

photoelectrode assembled with ionomer (Figure 2B) shows a bleary layer of ionomer over the Pt/CdS/CZTS/Mo electrode that was deposited from the ionomer dispersion. The presence of a three-phase boundary involving the photoelectrode, aqueous ionomer, and TL is required for this reaction. The amount of ionomer dispersion used was optimized to obtain the maximum photocurrent for hydrogenation of TL. Although the Pt/CdS/CZTS/Mo photoelectrode mostly works with the covered ionomer, the TL can access the Pt/CdS/CZTS/Mo photoelectrode surface. Figure 2A shows the bare Pt/CdS/CZTS/Mo photoelectrode, and the focus of the micrograph is clearer than that with the ionomer because of the absence of the insulating polymer layer. The CZTS layer consists of CZTS particles of varied sizes on the order of micrometers.

Current density–potential curves for the Pt/CdS/CZTS/Mo photoelectrodes are shown in Figure 3. Trace (a) in the figure
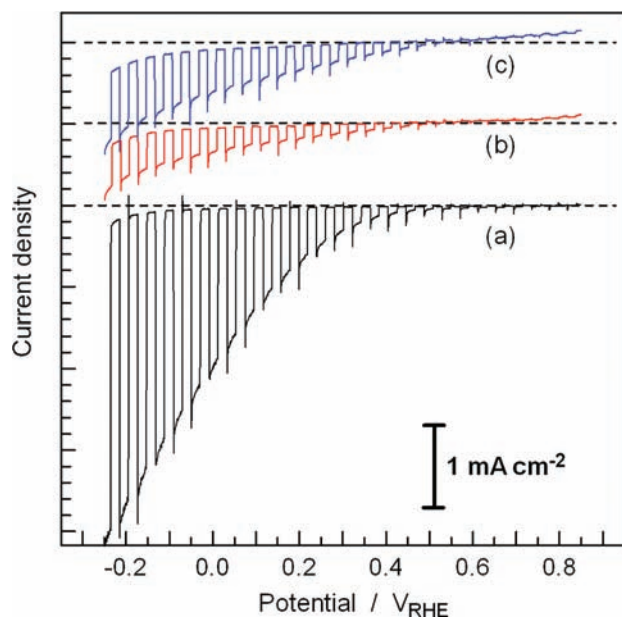
Figure 3. Current density–potential curves of Pt/CdS/CZTS/Mo photoelectrodes under intermittent irradiation by a 300 W Xe lamp with a cutoff filter ($\lambda > 420$ nm): (a) bare Pt/CdS/CZTS/Mo photoelectrode in 0.1 M Na_2SO_4/NaOH (pH 9.5); (b) Pt/CdS/CZTS/Mo assembly with the ionomer membrane in 0.1 M Na_2SO_4/NaOH (pH 9.5); (c) Pt/CdS/CZTS/Mo assembly with the ionomer membrane at the interface between TL and 0.1 M Na_2SO_4/NaOH (pH 9.5). The sweep rate was -5 mV s^{-1} (cathodic direction). The 0 mA cm^{-2} levels have been shifted vertically for clarity and are indicated by the dashed lines.

is for Pt/CdS/CZTS/Mo without the ionomer in 0.1 M Na_2SO_4/NaOH (pH 9.5). A cathodic photocurrent, which corresponds to hydrogen evolution from the photoelectrode, was observed below 0.7 V_{RHE}. The photocurrent density at 0 V_{RHE} was 2 mA cm^{-2}, which is equivalent to that reported previously. When Pt/CdS/CZTS/Mo was assembled with the ionomer and examined in 0.1 M Na_2SO_4/NaOH (pH 9.5) in both chambers, the photocurrent density at 0 V_{RHE} decreased to 0.3 mA cm^{-2}, as shown in Figure 1B without TL. This decrease was considered to be due to the decrease in the effective surface area resulting from the presence of the ionomer covering from the ionomer dispersion. This reduction in surface area is a problem in the double-phase electrochemical system. This could possibly be improved by further optimization of the assembly conditions. When the left chamber was filled with TL, the current potential curve changed, as shown by trace (c) in Figure 3. The current density at 0 V_{RHE} increased to 0.5 mA cm^{-2}, indicating that the Pt/CdS/CZTS/Mo photoelectrode assembled with the ionomer has higher photocurrent density at the TL–aqueous-electrolyte interface than in the aqueous electrolyte. One possible reason for this is that the reaction from TL to MC has lower energy (1.07 V) than water splitting (1.23 V). Thus, the reversible electrode potential is $+0.16$ V_{RHE} for hydrogenation of TL and 0 V_{RHE} for hydrogen evolution. A higher overpotential at the Pt cocatalyst can be expected for hydrogenation of TL than for hydrogen evolution, resulting in the observed higher photocurrent.

The time evolution of the current density at 0.2 V_{RHE} is shown in Figure 4 (blue curve, left axis). The current density
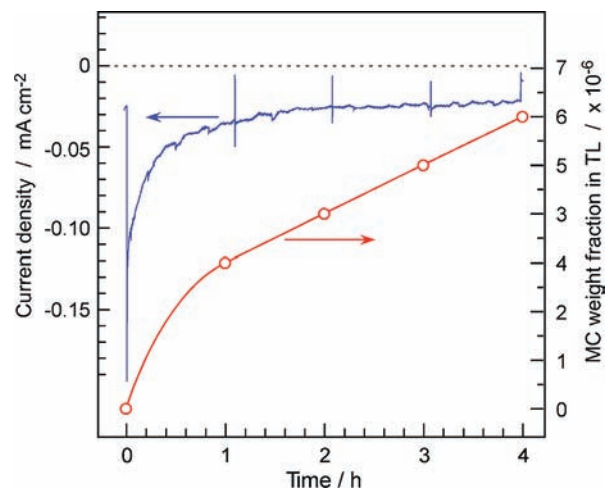
Figure 4. Current density and MC concentration as a function of reaction time for a Pt/CdS/CZTS/Mo assembly with an ionomer membrane at the interface between TL and 0.1 M Na_2SO_4/NaOH (pH 9.5) under continuous irradiation using a 300 W Xe lamp with a cutoff filter ($\lambda > 420$ nm). The potential was set to 0.2 V_{RHE} to suppress electrochemical (but not photoelectrochemical) MC production completely. The MC concentration was examined by GC. The spikes in the current–time curve were due to cutting off of the light for a short time every hour to confirm that the observed current was photocurrent.

decreased during the initial 1.5 h, but was almost constant (0.025 mA cm^{-2}) subsequently. The weight fraction of MC in TL was determined by GC, and this value is also plotted in Figure 4 (red curve, right axis). Every 1 h, the light was cut off for several seconds, and the disappearance of the photocurrent was confirmed. The total amount of synthesized MC was estimated to be 0.24 μmol from the GC analysis. The total charge of 0.16 C was obtained from the apparent area of the electrode and integration of the current density against time. Since TL hydrogenation is a six-electron reaction, the expected MC production from the number of electrons was 0.27 μmol. Thus, it was concluded that TL was photoelectrochemically hydrogenated in the present system with 88% faradaic efficiency.

The incident photon-to-current efficiency (IPCE) of the membrane/electrode assembly for TL reduction was examined with 680 nm monochromatic light, and a value of ca. 0.35% was derived at 0.2 V_{RHE} under irradiation. The observed IPCE needs to be drastically improved for a practical energy conversion system. To improve the system, further investigations of the morphology of the reaction field with multiple phases, the design of efficient semiconductor materials, and appropriate surface modifications are required.

The photocurrent for TL hydrogenation was observed to be in the same range as that for hydrogen evolution. This suggests the possibility of a direct TL-to-MC PEC system.

In conclusion, the conversion of TL to MC was successfully carried out using a PEC system with a Pt/CdS/CZTS/Mo photoelectrode assembled with an anion ionomer. This indicates that the conversion of TL to MC using the PEC system is an alternative candidate for solar energy conversion to chemical fuels after water splitting using a PEC system.

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Notes

The authors declare no competing financial interest.

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