

SHORT COMMUNICATIONS

Photocharging of Polynuclear Metal Complex at *n*-Cadmium Sulfide Photoanode Stabilized by Coating with Polymer-Pendant Tris(2,2'-bipyridine)ruthenium(II)

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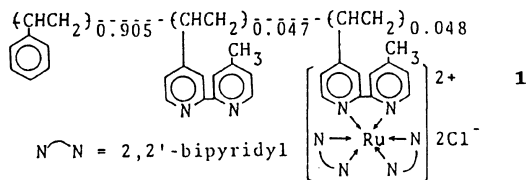
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Chemical storage of visible light energy is attracting much attention both in photoenergy conversion and information memory devices. Although some trials have already been reported on photoenergy conversion and storage with liquid-junction semiconductor electrodes,¹⁻⁵ further development of devices capable of directly storing light energy as chemical energy is one of the important and interesting topics in related research fields. In order to achieve this objective, the use of liquid-junction semiconductors should be the most promising approach. However, narrow bandgap semiconductors which can convert visible light energy, especially their *n*-type, have to be stabilized against photocorrosion when they are used as liquid-junction devices. One of the present authors has succeeded in stabilizing liquid-junction *n*-cadmium sulfide (CdS) by coating with polymer-pendant tris(2,2'-bipyridine)ruthenium(II) (Ru(bpy)₃²⁺) complex.⁶ This stabilized *n*-CdS is an excellent candidate to absorb and convert visible light energy into charges. As a storage material, Prussian Blue (PB) which is a mixed-valent high molecular weight polynuclear iron

cyanide complex (Fe³⁺₄[Fe^{II}(CN)₆]₃⁴⁻) was selected. Electrochemical properties of PB have well been characterized by Itaya and Neff.⁷⁻⁹ Since this complex has three kinds of reversible redox states, PB can store both positive and negative charges, so that it works as both the cathode and anode active materials of a secondary battery.¹⁰⁻¹² Moreover, PB can be used as a thin film, which allows its application to various devices. The distinct color change accompanying the reversible redox reactions suggests possible application to display devices. Photoelectrochemical studies of PB on *n*-TiO₂ have been reported.¹³ However, the reaction was induced only by ultra-violet light. Visible light-induced charging of PB is achieved by *n*-CdS photoanode stabilized by coating with polymer-pendant Ru(bpy)₃²⁺,⁷ and is reported in this paper.

Single crystalline *n*-CdS <0001> was stabilized⁶ by coating with a membrane of polymer-pendant Ru(bpy)₃²⁺ (1)¹⁴ by casting from DMF solution. The polymer coated CdS was dipped into an aqueous solution of RuO₄ (20 mg ml⁻¹), which gives rapid dispersion of



RuO_2 in the polymer membrane by reduction of RuO_4 . The characteristics of the *n*-CdS photoanode thus stabilized by the polymer coating containing RuO_2 dispersions have well been characterized in an aqueous electrolyte by cyclic voltammeteries.⁶ Both the Ru complex and RuO_2 in the polymer coating were required to stabilize the CdS photoanode dipped in an aqueous electrolyte containing halogen ions.⁶

Colloidal aqueous solution of PB was prepared by mixing equimolar (2 mM) amounts of $\text{K}^+ \text{[Fe}^{\text{III}}(\text{CN})_6]^{3-}$ and FeCl_2 . The aqueous PB solution was put into a two-compartment cell equipped with a cationic exchange membrane (Nafion) separator (each 0.8 ml), and the modified *n*-CdS and platinum counter electrodes were dipped into each compartment. After excluding air from the solution by bubbling argon gas for 30 min, the CdS was irradiated with visible light (intensity, 69 mW cm^{-2}) from a 500 W xenon lamp through cutoff filters (Toshiba VY-42 and IRQ-80) while continuing the argon gas bubbling.

During irradiation of the modified CdS, the color of both the PB solutions in the cell,

CdS/1 (RuO_2)/PB solution || PB solution/Pt, faded due to the photochemical reactions. Partial deposition of the photochemical products on the electrode surfaces was also observed, to be greenish brown at the CdS and white at the counter electrodes indicating that they are Berlin Green (BG, oxidized form of PB) and Prussian White (PW, reduced form of PB), respectively. After passing a theoretical photocurrent (0.077 C) corresponding to the equivalent amount of PB used in the solution, the visible spectra of both solutions were mea-

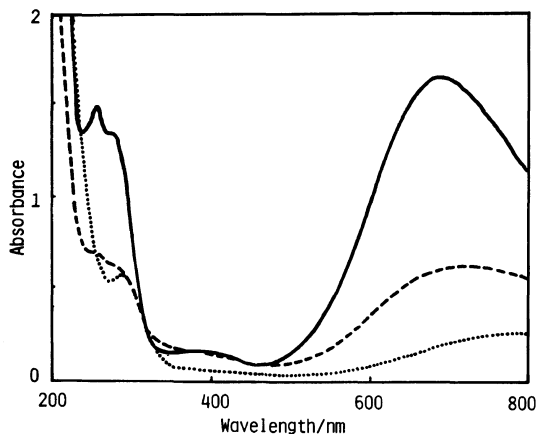


Figure 1. Visible spectra of the solution before (—) and after irradiation (---, CdS compartment; ·····, counter compartment).

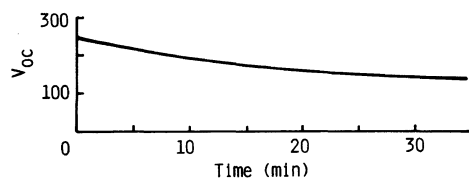


Figure 2. Time dependence of V_{oc} for a photocharged PB battery. Measured between two Pt electrodes dipped in each compartment.

sured and are shown in Figure 1. These results show clearly that PB was oxidized in the CdS compartment to give BG and reduced in the counter electrode compartment to give PW.

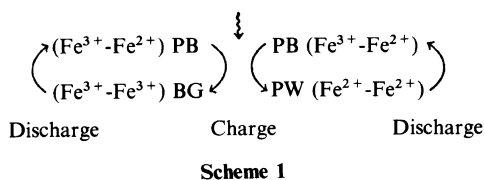
PB was thus charged photochemically giving the oxidized form at the stabilized *n*-CdS and reduced form at the counter electrode. After the charging, an open-circuit voltage of 250 mV was obtained between the counter electrode and platinum electrode dipped into the CdS compartment. Under open circuit conditions this voltage is kept fairly stable (Figure 2) indicating that the photocharged state can be maintained. By short-circuiting these two platinum electrodes, the BG and PW returned to the original PB as confirmed by visible spectroscopy. Although the cell can be charged photoelectrochemically and discharged in the dark repeatedly, the reversi-

Table I. Cells for PB photocharging^a

System	Type	Composition
1	Solution	CdS/1, RuO ₂ /PB soln. PB soln./Pt
2	Solution/Membrane	CdS/1, RuO ₂ /PB soln. aq. electrolyte/PB membrane/NESA
3		CdS/1, RuO ₂ /PB membrane/aq. electrolyte/PB membrane/NESA
4	Solid	CdS/1, RuO ₂ /PB membrane PB membrane/NESA

^a ||, Separator (Nafion film).
aq. electrolyte = 0.5 M KNO₃.

bility of the photocharge/dark-discharge was not so high because of the partial deposition of the charged products (PW and BG) on the electrodes. Although the V_{oc} (250 mV) obtained after the photocharging is lower than the theoretical value of 690 mV¹¹ and the reversibility of the present preliminary system is still not so high, the photocharging and dark discharging of PB battery has thus been confirmed (Scheme 1).



PB was coated on a Nesa glass counter electrode or on the 1-modified CdS by reductive deposition in an aqueous solution of BG with -0.5 V vs. SCE applied potential as reported.^{8,9} The cells for PB photocharging composed of PB solution and/or PB film are shown in Table I. For the PB solution and PB membrane coated on the NESA glass, photocharging of PB was confirmed by visible spectroscopy as shown in Figure 1. For the PB membrane coated on modified CdS, photocharging was observed only by its color change from blue to greenish brown. The photocharge and dark discharge of the system 1 composed

of PB solution is already described above. The system 2 composed of PB solution/PB membrane showed almost the same photocharge and dark discharge as system 1. For systems 3 and 4 which involve PB-coated CdS, only the photocharge was studied since these systems are not equipped with discharge electrodes at the PB/CdS. The design of a discharge electrode at the PB-coated CdS is now under way to fabricate a stable photocharge/dark-discharge device composed of both PB membranes.

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