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COMPARATIVE MEASUREMENTS OF PHOTOCURRENT QUANTUM EFFICIENCY: FLUOROMETRIC, THERMOMETRIC AND ACTINOMETRIC METHODS APPLIED TO A FLUORESCENT POLYCRYSTALLINE ZnO ELECTRODE

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The three methods in the title were directly compared by using an electrode made of luminescent Cu^{2+}-doped ZnO. The values of the quantum efficiency as measured by the three methods were in good agreement. The feasibility of the methods is briefly discussed.

The conversion of solar energy into electrical and/or chemical energy in a photoelectrochemical cell using a semiconductor electrode has been studied in depth.[1-3] In such a system the quantum efficiency of a semiconductor electrode in a photoelectrochemical cell is a determining factor for the effective utilization of solar energy.[4,5]

Usually the quantum efficiency is measured by the photon counting (actinometric) method. Recently we have developed a new method to determine the "intrinsic" quantum efficiency by the measurement of the temperature change of a semiconductor electrode surface with a thermistor.[6-9] This method is applicable even to a reflective semiconductor because only the absorbed light quanta contribute to the temperature change.

Recently Ellis et al.[10,11] have reported a new fluorometric method to measure the quantum efficiency of luminescent semiconductors, such as Te- or Ag-doped CdS. This method is simple and useful as long as a luminescent semiconductors can be prepared.

In the present work we prepared luminescent polycrystalline ZnO electrode, and by using it confirmed that the three methods (photon counting or actinometric method, temperature change or thermometric method, and fluorescence change or fluorometric method) gave the same result.

For preparation of fluorescent ZnO, pure ZnO powder (Koso Chemicals, reagent grade) was doped with Cu^{2+}. A prescribed volume of copper nitrate (Yoneyama Chemicals, reagent grade) aqueous solution was added to a given amount of the ZnO powder. After mixing and drying, the ZnO powder was pressed into a pellet (18 mm diameter and 2 mm thick) under 150 kgf/cm^2 (1 kgf=9.81 N). The pellet of ZnO was then heated in an electric furnace at 1300 °C for 3 h in the air.

The top face of the pellet was used as the electrode surface. A copper lead

wire was fixed to the bottom with silver paste through an In-Ga ohmic contact. The pellet was covered with epoxy resin except the electrode surface.

i) Fluorometric method

The arrangement of a pyrex cell for in situ fluorescence measurements on a fluorescence-phosphorescence spectrometer (Hitach MPF-4) is shown in Fig. 1. The fluorescent ZnO electrode was fixed to one side of the cell with epoxy resin as shown in Fig. 1.

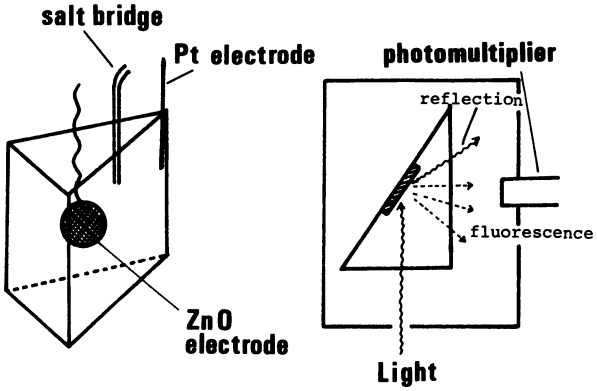

Fig. 1. In situ fluorescence measurement.

ii) Thermometric method

The measurement of temperature change of the fluorescent ZnO polycrystalline electrode was carried out according to the method previously reported.[6-9] The temperature change of the electrode was measured during a 10 s pulse of the monochromatic light at 340 nm obtained by using an interference filter. Photothermal responses were obtained for the ZnO electrode in the electrolyte solution during anodic polarization and under open circuit conditions. The corresponding current and temperature change were then plotted as a function of the anodic potential. The apparatus and the thermistors used were the same as those reported in the previous papers.[6,7]

iii) Actinometric method

The number of incident photons was measured by the chemical actinometric method using potassium trioxalatoferrate(III).[12] By comparison with the number of electrons flowing in the photoelectrochemical cell, the quantum efficiency was calculated.

Fluorescence characteristics of polycrystalline ZnO

Cu^{2+}-doped polycrystalline ZnO (Cu^{2+} mass fraction, 2.5×10^{-5}) gave a broad fluorescence spectrum peaking at 510 nm. The efficiency of fluorescence was about 1%, so that the flurescence process does not appreciably affect the photoelectrochemical reactions of the ZnO. The fluorescence was strongest by 340 nm excitation, and in separate experiments we confirmed that photooxidation of the ZnO electrode ($ZnO + 2p^{+} \longrightarrow Zn^{2+} + \frac{1}{2}O_2$) also occurred at this wavelength.

Fluorescence change with applied potential and determination of quantum efficiency

The current-potential behavior with and without irradiation is similar to that observed for undoped ZnO.

The fluorescence intensity of the ZnO electrode was almost the same both in an electrolyte and in the air. However, when the ZnO electrode was anodically polarized, the intensity of fluorescence decreased (Fig. 2), and the decrease of the fluorescence intensity depended on the applied potential.

When N electrons are excited by the incident photons and a fraction ϕ of these electrons flow out of the electrode into the external circuit, the remaining $N(1 - \phi)$ electrons will decay through the radiative and non-radiative transitions. The intensity I of the observed fluorescence is proportional to the number of the electrons that undergo the radiative transition, so that in the steady state

$$N(1 - \phi)\eta = \alpha I \quad (1)$$

where α is a constant and η is the probability of the radiative transition. With the external circuit open ($\phi = 0$) and the other conditions being the same,

$$N\eta_o = \alpha I_o \quad (2)$$

The subscript $_o$ means the open-circuit condition. It appears reasonable to assume that $\eta_o = \eta$, then

$$\phi = \frac{I_o - I}{I_o} \quad (3)$$

Hence the quantum efficiency of the photocurrent can be determined by measuring the fluorescence intensities under open-circuit and closed-circuit conditions.

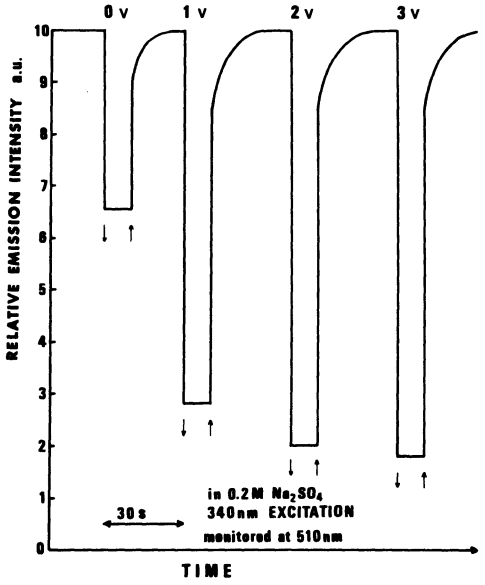

Fig. 2. Decrease of fluorescence intensity with applied potential.

Quantum efficiency from the thermometric method

The fluorescence efficiency of the ZnO electrode employed was too low (less than 1%) to interfere with the thermometric measurement of the quantum efficiency. For this measurement, the following equation holds in the limiting photocurrent region;[6]

$$E\frac{\Delta T}{\Delta T_o} = K + e\phi(V - V_{fb}) \quad (5)$$

where E is energy of incident monochromatic light pulse; ΔT, temperature change, ΔT_o, temperature change in the open circuit condition; ϕ, quantum efficiency; V, applied potential vs. a reference electrode; V_{fb}, flatband potential vs. the same reference electrode; e, the elementary charge; and K, constant.

In accordance with the equation(5), values of $E\frac{\Delta T}{\Delta T_o}$ are plotted against potential V in Fig. 3 for the fluorescent ZnO electrode, where the illumination condition is λ = 340 nm and t = 10 s . The quantum efficiency of the photocurrent was determined from the slope of the straight line in the limiting photocurrent region.

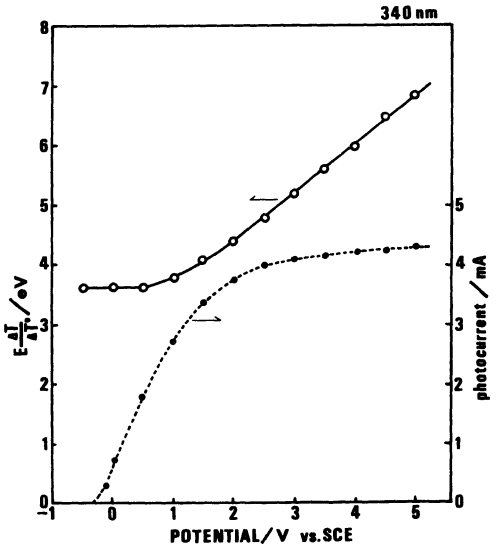

Fig. 3. Normalized temperature change and photocurrent.

Quantum efficiency from the usual actinometric method

The number of incident photons of 340 nm monochromatic light was measured by means of the actinometry with potassium trioxalatoferrate(III). The quantum efficiency of the photocurrent was then calculated from the ratio of the number of electrons flowing to the number of incident photons.

Table 1 Comparison of quantum efficiency of the photocurrent at 3.0 V (vs. SCE).

	quantum efficiency
fluorometric method	0.82
thermometric method	0.80
actinometric method	0.80

The values of the quantum efficiency of the ZnO electrode at 3.0 V vs. SCE are in excellent agreement as shown in Table 1.

For a semiconductor with a weak fluorescence, the fluorescence method is the most convenient, although it is not easy in general to find such a semiconductor. If the quantum efficiency is equal to or larger than a few percent, the temperature method is also suitable for obtaining the quantum efficiency, even for semiconductors which have reflective surfaces. When the quantum efficiency is very small, say, less than a few percent, the actinometric method must be used, because in this method the number of electrons can be calculated from the current over a wide range of values independent of the number of incident photons.

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