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Review

Electrochemical measurements of molecular compounds in homogeneous solution under photoirradiation

Arisa Fukatsu [a], Mio Kondo [a,b,c], Shigeyuki Masaoka [a,b,*]

[a] Department of Life and Coordination-Complex Molecular Science, Institute for Molecular Science, 5-1, Higashiyama, Myodaiji, Okazaki, Aichi 444-8787 Japan
[b] Research Center of Integrative Molecular Systems (CIMoS), Institute for Molecular Science, 38, Nishigo-naka, Myodaiji, Okazaki, Aichi 444-8585 Japan
[c] ACT-C, Japan Science and Technology Agency (JST), 4-1-8, Honcho, Kawaguchi, Saitama 332-0012 Japan

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ABSTRACT

Photochemical reactions are crucial chemical reactions not only in biophysical processes, such as photosynthesis and phototransduction, but also in technological applications, such as artificial photosynthesis and optogenetics. To understand the mechanisms of photochemical reactions, which involve initial photoexcitation and subsequent chemical processes, analytical techniques to evaluate the properties and reactivities of photochemically generated intermediates are highly important. In this review, photoelectrochemical techniques that enable electrochemical measurements of molecular substrates such as transition metal complexes and organic compounds in homogeneous solution under photoirradiation are summarized. First, we introduce four photoelectrochemical systems developed in the 1960–80s: photopolarography, the rotating photoelectrode technique, the flow cell system and photomodulation voltammetry. Next, a recently developed system for cyclic voltammetry under photoirradiation is described. We hope that this review will contribute to the further development and improvement of photoelectrochemical measurement systems for molecular substrates.

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1. Introduction

Photochemical reactions of organic compounds [1–3] and transition metal complexes [4–6] have been widely studied not only because of their fundamental importance in chemistry but also because they serve as model reactions of biophysical phenomena such as photosynthesis [7,8] and phototransduction [9,10]. In addition, a detailed understanding of the mechanisms of such photochemical reactions would provide deeper insight into future technological applications including artificial photosynthesis [11–13] and optogenetics [14,15]. Because a photochemical reaction consists of an initial photoexcitation process and subsequent multistep exothermic processes, analyzing the intermediates generated during the reactions is essential to understanding the mechanisms of photochemical reactions of molecular compounds.

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* Corresponding author at: Department of Life and Coordination-Complex Molecular Science, Institute for Molecular Science, 5-1, Higashiyama, Myodaiji, Okazaki, Aichi 444-8787 Japan.

E-mail address: masaoka@ims.ac.jp (S. Masaoka).

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Electrochemical measurements, *e.g.*, cyclic voltammetry, are a well-established analytical means to evaluate the HOMOs and LUMOs of molecular substrates by observation of the electrical current attributed to electron transfer between the substrates and the electrode [16]. Because the electronic structures of the substrates change upon photoexcitation, *in situ* observation of the electrochemical response of the substrates under photoirradiation can be a powerful technique to investigate the photochemical reaction mechanisms. However, electrochemical analyses under photoirradiation for molecular substrates in homogeneous solution are not widely performed at present, although those for heterogeneous systems have been extensively used in the fields of solar cells and semiconductor photocatalysts [17–19].

From a historical point of view, electrochemical analyses under photoirradiation for molecular substrates in homogeneous solution are not an unexplored research topic. The first pioneering work on such measurements, photopolarography, was reported in 1960, by using a dropping mercury electrode as the working electrode, as described in Chapter 2.1 [20–43]. In the 1970s, the special rotating electrode, composed of an inert-metal ring electrode and an optically transparent disk, was developed and used to detect the electrochemical responses of photochemically generated intermediates (Chapter 2.2) [20,44–52]. In the 1980s, flow cell systems were developed to detect the small amount of molecules in solution (Chapter 2.3) [53–77]. In the same period, by adopting the modulation principle in photoelectrochemical measurements, a technique called photomodulation voltammetry was also developed to detect the redox current of short-lived transient species (Chapter 2.4) [78–91]. In addition, cyclic voltammetry under photoirradiation has recently been demonstrated by using a thin layer technique (Chapter 2.5) [92,93]. These photoelectrochemical techniques were separately developed by different research groups in different periods by using different experimental setups (Table 1), although they were developed with a common objective, to some extent.

The purposes of this review are (1) to describe the photoelectrochemical techniques to demonstrate electrochemical measurements of molecular substrates in homogeneous solution under photoirradiation, (2) to compile the relevant knowledge in the literature, and (3) to lay a foundation for further progress in this field of research. After introducing the four photoelectrochemical systems developed in the 1960–80s, we describe a recently developed system that enables cyclic voltammetry under photoirradiation. In this review, we will focus only on the electrochemical measurements of molecular substrates in their photoexcited states or those formed after photoexcitation of molecules, and will not describe the measurements of molecular substrates reduced by the electrons generated by the photoirradiation to the electrode (*i.e.* electron-photoinjection experiments [94]). We will then conclude by discussing future work in this field.

2. Photoelectrochemical systems for homogeneous solutions

2.1. Photopolarography

The research on electrochemical measurements of molecular substrates in solution under photoirradiation began with the detection of the photocurrent attributed to photochemically

Table 1
List of photoelectrochemical systems used to perform electrochemical measurements of molecular substrates in homogeneous solution under photoirradiation.

Chap.	Photoelectrochemical System	Period	Working electrode	Light	Target[a]
2.1.	Photopolarography	1960s–	Dropping mercury electrode	Continuous/pulse	A
2.2.	Rotating photoelectrode technique	1970s–	Planar electrode	Continuous	A
2.3.	Flow cell system	1980s–	Planar electrode	Continuous/pulse	A
2.4.	Photomodulation voltammetry	1980s–	Planar electrode	Pulse	B, C
2.5.	Cyclic voltammetry under photoirradiation	2010s–	Planar electrode	Continuous	A, B

[a] A: detection of intermediates/products of photochemical reactions, B: analysis of redox potentials of transient species, C: analysis of lifetimes of transient species.

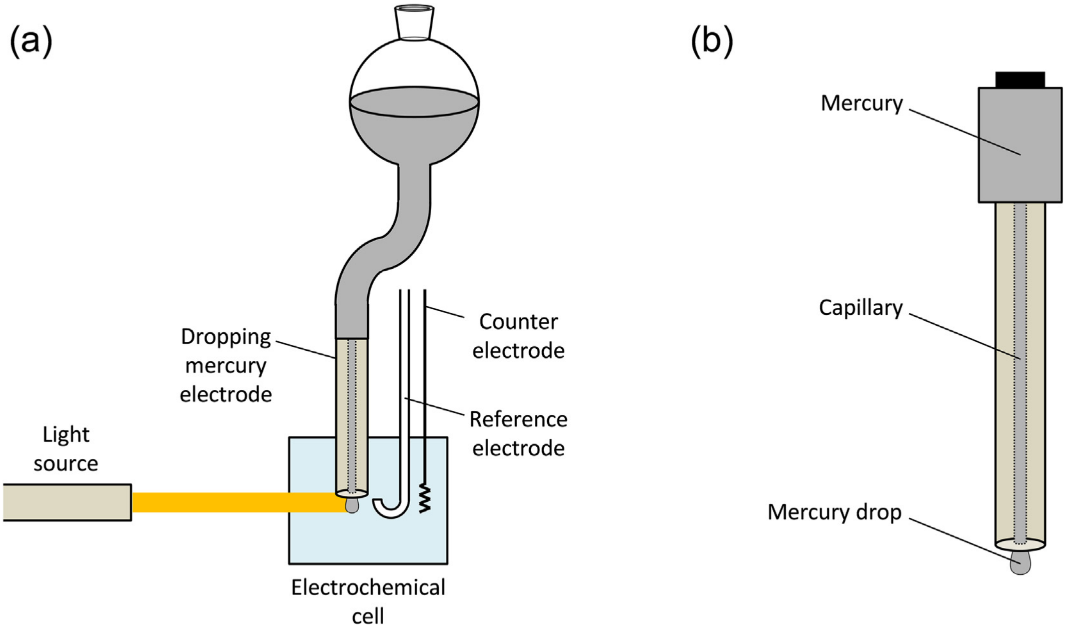

Fig. 1. (a) A typical experimental setup for photopolarography measurements. (b) A schematic illustration of a hanging mercury drop electrode (HMDE).