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Spectroelectrochemical studies on redox reactions of eosin Y and its polymerization with Zn^{2+} ions

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ABSTRACT

Redox reactions of eosin Y (EY) in aqueous solutions in the presence and absence of Zn^{2+} were studied by spectroelectrochemical measurements combining cyclic voltammetry and in situ monitoring of absorption spectra, employing an optically transparent thin layer electrode (OTTLE). In the absence of Zn^{2+}, the original dianion, EY^{2-}, undergoes one electron reduction to trianion radical that is stable above pH 11, but is protonated and doubly reduced under the lower pH to become highly stabilized against re-oxidation. When Zn^{2+} is present, the reduction occurs as a two electron process coupled with complexation of two Zn^{2+} ions to bridge eosin Y molecules, resulting in polymeric mixed aggregates that are also greatly stabilized against re-oxidation. This reaction has been identified as the key process in the electrochemical self-assembly of ZnO/eosin Y hybrid thin films in nanowire structures. On the other hand, two electron oxidation of EY^{2-} was found to convert the molecule into lactone form which is strongly stabilized against re-reduction. Despite of such highly complex redox reactions, these processes in overall were found to be reversible both electrochemically and spectroscopically.

1. Introduction

About a decade ago, we found a phenomenon of self-assembled electrochemical growth of nanostructured crystalline ZnO thin film hybridized with eosin Y by simply adding eosin Y into the bath for cathodic electrodeposition of ZnO, either aqueous solution of $Zn(NO_3)_2$ [1–3] or $ZnCl_2$ saturated with O_2 [4,5]. We named the process as "electrochemical self-assembly (ESA)" that can be utilized as a new methodology to obtain inorganic/organic hybrid materials [6]. Eosin Y is loaded into the film as solid in a nanowire structure with a diameter of about 10 nm vertically aligned to the electrode plane. It is totally phase separated from ZnO and thus could be completely removed from the hybrid film by dipping the film in a dilute alkaline without dissolving ZnO. On the other hand, ZnO domains connect each other to retain perfectly crystalline structure. Thus, such a process results in a formation of ZnO in a "porous crystalline" structure having high surface area as well as high crystallinity in the same body [6] (see Supporting information Fig. 1S for SEM pictures of the electrodeposited porous crystalline ZnO). Such porous crystal ZnO layer turned out to be very useful as the photoelectrode material in dye-sensitized solar cells (DSSCs), achieving an incident photon to current conversion of about 90% and an energy conversion efficiency of 5.6% when combined with a suitable photosensitizer dye [6–8]. The process is especially useful for realization of low cost and light weight plastic solar cells as it needs neither high temperature nor aggressive chemicals, unlike the traditional method for preparation of porous electrode based on high temperature sintering of metal oxide nanoparticles. Also, design flexibility of the nanostructure in the process of ESA gives us a large room of further improvement of the property. Therefore, understanding the mechanism of hybridization between ZnO and eosin Y is highly important for the development of the related technologies.

Loading of eosin Y molecules into ZnO matrix is enhanced when eosin Y is electrochemically reduced [9]. In our previous study, we carried out electrochemical analysis for reduction of eosin Y in aqueous mixed solutions of KNO_3 and $Zn(NO_3)_2$ [3]. From the linear shift of the reduction potential with respect to $\log[Zn^{2+}]$, formation of complex between reduced eosin Y and Zn^{2+} in a stoichiometric ratio of 1:1 was found. However, the number of electron involved in the reduction of a single eosin Y molecule was naively assumed to be one, thus a complex between singly reduced eosin Y and one Zn^{2+} ion, because of the lack of information about the amount of dye per consumed charge. In fact, redox chemistry of xanthene dyes including eosin Y has been a matter of numerous studies [10–12]. In some cases, a single electron process was proposed, while others suggested a two electron process. Such a confusion was caused by the change of pH of solutions they employed, as it is evidently shown later in this paper.

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We have then coupled in situ UV–Vis absorption monitoring and cyclic voltammetry employing an optically transparent thin layer electrode (OTTLE) to combine information about redox potential, charge and spectral change for a finite amount of eosin Y in the OTTLE, in order for us to be able to ascertain the stoichiometry of the reaction. A part of the results for the reduction process was published in 2009 [6]. It was found that dianion of eosin Y (hereafter to be denoted as EY^{2-}) was reduced to a singly reduced radical anion ($EY^{3\bullet-}$) having an absorption peak at 407 nm only under a highly alkaline environment. In the presence of Zn^{2+}, this signal of the anion radical completely vanished and the number of electron changed to two, ending up with a product complex of $(EY^{4-})(Zn^{2+})_2$ which was strongly stabilized against reoxidation. Subsequent to our previous communication [13], Goux et al. have performed similar experiments and succeeded to confirm the conclusions [14]. In addition they carried out in situ electron spin resonance (ESR) spectroscopy and mass spectroscopic (MS) analysis of the product, confirming a singly reduced semiquinone radical in the absence of Zn^{2+} and a complex between reduced eosin Y and Zn^{2+} in its presence, respectively. However, it was not possible to clarify the stoichiometry of the reaction. Even though a two electron reduction of EY^{2-} and its complex formation with one Zn^{2+} ion was already suggested, a quantitative treatment of the electrochemical data was hindered by a parallel H_2 evolution at the Pt working electrode. Further, the resolution of the UV–Vis spectra was too low to differentiate between the different species [15].

In this paper, we present a comprehensive study on redox reactions of eosin Y under different pH and in the presence and absence of Zn^{2+} by means of in situ UV–Vis absorption spectroscopy employing an OTTLE whose gap was chosen small enough to allow complete redox changes of eosin Y molecules. By use of ITO electrodes having a high overpotential for proton reduction and a high concentration of supporting electrolyte for effective charge compensation to prevent change of eosin Y concentration in the OTTLE, thermodynamically well regulated redox peaks were produced in the cyclic voltammograms despite of the non-ideal geometry of the electrode. This way, we were able to count the charge consumed for each redox reactions and compare it to the quantity of eosin Y that underwent the reaction. Also, shift of redox potentials on pH and log$[Zn^{2+}]$ could be determined to fully elucidate the stoichiometry of each redox step.

Before going into the following sections of this paper, it is also important to note that we ambitiously try to illustrate reactions in full chemical structures of eosin Y and its complexes, not all of which, however, are fully supported from our own experiments and knowledge from literature. Some of them may appear highly speculative. However, we still try to visualize the most likely dominant reaction to match our observation and to be consistent with the stoichiometry of the reaction that we confirmed from our experiments. Because the series of redox reactions of eosin Y is highly complex and involve polymerization in indefinite structures in some cases, precise description of reactions in simple formulae is in fact impossible. The authors would like the readers to see the postulated reaction scheme as a sort of guide for the future studies employing any other spectroscopic measurements else than UV–Vis absorption, either to approve or disapprove the structures suggested from our best knowledge at the present.

2. Experimental

Eosin Y disodium salt ($EYNa_2$, Kanto), $ZnCl_2$ (Merck) and KCl (Merck) were of commercially available purest grade and used as purchased without further purification. Milli-Q pure water was used throughout the experiments. Indium tin oxide (ITO) coated conducting glass (10 Ω/sq., thickness = 1.1 mm, Musashino Fine Glass) and fluorine doped SnO_2 (FTO) coated conductive glass (10 Ω/sq., thickness = 1.1 mm, Asahi glass) were ultrasonically cleaned subsequently in 2-propanol, acetone and water. FTO conducting glass substrate was etched in a 45% HNO_3 solution for 2 min to activate the surface of electrode. Glassy carbon (GC) electrode was also used for some experiments that was polished by a downy cloth and rinsed ultrasonically in water before use.

The cell for spectroelectrochemical measurements was configured as shown in Fig. 1. An electrochemical cell in a 2 × 2 × 4 cm size made of optical quartz plates was prepared. Three electrodes, an optically transparent thin layer electrode (OTTLE) as a working, a saturated calomel electrode (SCE, Yanaco MR-P2A) as a reference and a Pt wire as a counter are placed in the cell to allow the monitoring light beam to go through the OTTLE without being hindered by the other objects. The OTTLE was configured from an ITO glass plate cut in a 8 × 30 mm size and a slide glass (thickness = 0.8 mm, Matsunami) cut in a 8 × 20 mm size. These two plates sandwich two small strips of Naflon films (thickness = 60 μm) placed at the top and the bottom of the slide glass with the ITO conductive side facing inside of the thin layer. They are bound together by using PTFE seal tape (Nichias corp.). Care was taken to leave approximately 2 mm from the bottom of the OTTLE open, so that the sample solution could be introduced to the gap by capillary action. This way, an OTTLE with a gap of approximately 60 μm could be prepared. However, the exact gap distance was calculated from the absorbance of a sample solution with a known concentration to determine the amount of eosin Y within the OTTLE.

The samples were aqueous solutions containing 0.5 mM $EYNa_2$ and KCl as supporting electrolyte. $ZnCl_2$ was added at variable concentrations up to 100 mM to study the influence of Zn^{2+}. The concentration of the supporting electrolyte was 0.1 M for standard CV measurements using a flat ITO electrode open to the sample solution but was 1.0 M for the measurements employing the OTTLE to assure exchange of the electrolyte between the narrow gap of the OTTLE and the bulk solution at the bottom of the cell. Mixtures of KCl and NaOH were also used as the supporting electrolyte for measurements under high pH while maintaining the ionic strength constant. The solutions were deaerated by bubbling Ar gas prior to the measurements and the gas was flown through the cell during the measurements to avoid contamination of current with that for O_2 reduction.

The spectroelectrochemical cell was put in a cell holder equipped with two optical fibers, which were connected to an Otsuka Electronics MCPD-7000 diode-array type multichannel spectrophotometer for monitoring absorption spectra. Potential scanning and current monitoring were performed using a Hokuto Denko HSV-100 voltammetric analyzer. The rate of potential scanning was 2 mV s^{-1} for the spectroelectrochemical measurements. The potential scanning was initiated from the equilibrium potential into negative direction in all measurements. Each spectrum was measured with a sampling time of 20 ms and 5 times accumulation. Spectral data were acquired with an interval of 5 s, thus corresponding to 10 mV interval on the potential scale.

As we could estimate the total amount of eosin Y in the OTTLE from the initial absorption spectrum, we could calculate the molar fraction that underwent redox reactions from the spectral change using Lambert–Beer's law. On the other hand, integration of peak charge in the CV gave the amount of charge exchanged in each redox reaction. Comparison of these data therefore yielded number of electron involved in the redox reaction of a single eosin Y molecule. In each measurement, the area of the OTTLE in contact with the sample solution was measured to convert the measured current into current density. The ITO glass and slide glass were assumed to be parallel, thus in a constant gap, for determination of the amount of eosin Y in the OTTLE.