Appling plasmonics based electrochemical microscopy to thin-layer electrochemistry ☆

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ABSTRACT

Plasmonics based electrochemical microscopy (PECM) has been introduced to image local electrochemical reactions optically. The algorithm used to convert the plasmonic signal to current, however, is not applicable to thin-layer electrochemistry, which is important for microfluidic detection and biosensing applications. Here we introduce a PECM algorithm for both semi-infinite and thin-layer electrochemical geometries. The new algorithm expresses plasmonic signal as local concentration of redox species on the electrode surface, which, together with the diffusion and Nernst equations, determines the current. We validate the algorithm experimentally by fabricating a thin-layer electrochemical cell, consisting of two-parallel electrodes separated with various distances.

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1. Introduction

Electrochemical (EC) detection is a powerful analytical tool with broad applications [1–5]. Recently, plasmonics based electrochemical microscopy (PECM) has been developed to image local EC reactions on an electrode surface optically via surface plasmon resonance (SPR) [6]. Compared to Scanning Electrochemical Microscopy (SECM) [7,8], PECM allows imaging of heterogeneous surface reactions with fast speed (<1 ms per image). PECM has been applied to studying various electrochemical processes. Examples include local cyclic and square wave voltammograms, electrocatalytic reactions of single nanoparticles, and local charge impurities in monolayer graphene [9–11].

Although successful, PECM assumes a semi-infinite boundary condition, which is not applicable to thin-layer electrochemistry. Thin-layer electrochemistry is important for EC detections of chemical and biological species in microfluidic devices [12–18], and extension of PECM to thin-layer EC systems is thus necessary. In this work, we introduce a new algorithm that works for both semi-infinite and thin-layer EC geometries, validate the algorithm experimentally by fabricating thin-layer EC cells with different thicknesses, and compare the results with simultaneously recorded cyclic voltammograms (CVs) with the conventional electrochemical method.

2. Experiments

2.1. Reagents

All chemicals were purchased from Sigma-Aldrich and used without further purification. 0.2 M sodium fluoride (NaF) solution was prepared with deionized water (18 M Ohms.cm). 0.5, 2, 5, and 10 mM ferricyanide/ferrocyanide ($Fe(CN)_6^{3-/4-}$) solutions were prepared by dissolving 1:1 M ratio of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ in the 0.2 M NaF solution.

2.2. Imaging system

A prism-based plasmonic imaging setup [19–22] was used for all experiments described in this paper. The optics of the imaging system has been discussed in details previously [21–23]. Briefly, a collimated p-polarized red LED (Hamamatsu L7868-01) was used as light source, which was directed through a BK7 prism onto a gold-coated glass coverslip placed on top of the prism via index matching oil. Light reflected from the gold film was imaged by a high-speed CCD camera (Pike F-032B from Allied Vision Technologies, Newburyport, MA 01950).

2.3. Preparation of thin-layer EC cells

The gold-coated coverslips (VWR no. 48366045) also served as the working electrode (WE) in the thin-layer EC cell, which was prepared by thermal evaporation in a high vacuum chamber (Edwards II). Prior to gold evaporation, each glass coverslip was cleaned with absolute ethanol followed by rinsing it with deionized water. The cleaned glass coverslip was coated with 1.6 nm-chromium, and then with 47 nm-gold. The thin-layer EC cell was fabricated by coating a patterned PDMS film

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☆ This paper is dedicated to Prof. Hongyuan Chen on his 80th birthday
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on the gold-coated glass coverslip using sol-gel spin coating and thermal annealing. The patterned PDMS film served as a gasket, on which another gold-coated coverslip was placed (as the top electrode). The thickness of the PDMS film was controlled by changing the spin coating rate (i.e., 1000 rpm, 2500 rpm, and 3000 rpm), which allowed us to prepare EC cells with different electrode separations.

2.4. Electrochemical measurement

A potentiostat (microAutolab type III) was used to control the potential of the top and bottom electrodes, and record the EC current. The bottom electrode served as the working electrode (WE), which was imaged with PECM. The top electrode was connected to the reference (RE) and contour electrodes (CE) (Fig. 1a). For the semi-infinite EC cell, a Pt wire (CE) and Ag/AgCl (RE) were immersed into a PDMS EC well as counter and reference electrodes, respectively. To synchronize the plasmonic and conventional EC measurements, the potential and current from the potentiostat were recorded with an A/D board (NI USB-6210, from National Instruments, Austin, TX 78759) along with the open shutter trigger signal from the CCD camera by a MATLAB program.

2.5. Calibration

To determine PECM current, we performed calibration to relate current density to SPR angular shift [23]. This was carried out by measuring SPR and EC with different concentrations of the redox species (2 mM, 5 mM, and 10 mM) with a 40 μm-EC cell. The calibration factor was found to be 0.6 A/m²-mDeg. Note that in PECM, we tuned the incident angle of light near SPR angle, and measured the reflected light intensity, which is proportional to the SPR angular shift over a certain angular range [23].

3. Results and discussion

3.1. PECM algorithm

PECM reported to date [23] assumes an EC cell with a semi-infinite boundary condition [24] (Fig. 1(b)). This condition is not applicable to thin-layer electrochemistry because the electrode opposite to the working electrode has a non-negligible effect on electrochemical processes taking place on the working electrode (Fig. 1(c)). To develop a more universal PECM, we remove the constraint of semi-infinite boundary condition, and consider a thin-layer EC cell, consisting two parallel plate electrodes. The plasmonic signal is proportional to the local concentration of redox species on the working electrode surface, which is treated as a boundary condition. We further assume thermal equilibrium, which leads to the Nernst equation, providing an additional boundary condition. By solving diffusion equations, together with the boundary conditions, we determine the local current density with the finite element analysis (COMSOL Multiphysics). We present the algorithm with greater details below.

As we have shown previously [6,23], if the diffusion distance is much larger than $l \sim 200$ nm, the decay distance of the evanescent field associated with SPR, the SPR angle can be expressed by

$$\theta(t) \approx B\left[\alpha_O C_O(z,t)|_{z=-\frac{L}{2}} + \alpha_R C_R(z,t)|_{z=-\frac{L}{2}}\right],\tag{1}$$

where $C_O(z,t)|_{z=-\frac{L}{2}}$ and $C_R(z,t)|_{z=-\frac{L}{2}}$ are the concentrations of the oxidized and reduced molecules near the working (bottom) electrode, α_O and α_R are the changes in the local refractive index per unit concentration for the oxidized and reduced molecules, respectively, and B is SPR angle shift per unit change in the bulk index of refraction. The diffusion distance is $\sqrt{Dt}$, where t is the time scale of measurement, which scales with the time requires for one potential cycle in cyclic voltammetry. Typical diffusion coefficients of ions and molecules in aqueous solutions
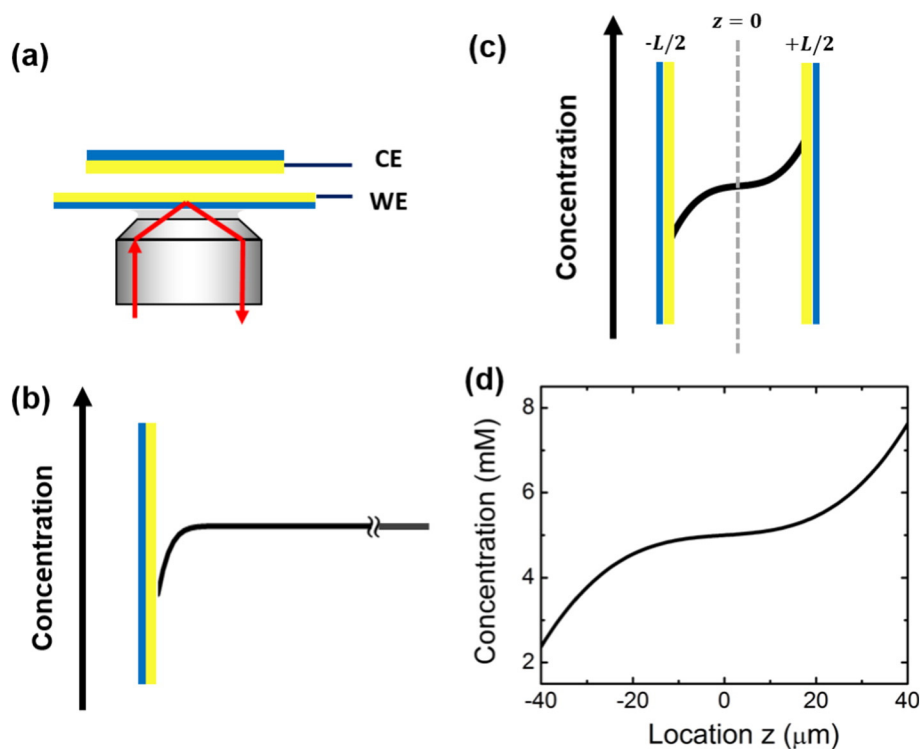

Fig. 1. Schematics of thin-layer electrochemical cell, and concentration distributions. (a) Experimental setup. (b) and (c) Schematic of concentration distributions with semi-infinite and thin-layer electrochemical cells. (d) Simulated concentration distribution. The simulation was performed with $E(-\frac{L}{2}) = -E(+\frac{L}{2}) = -0.15$ V and electrode separation of 80 μm.