

SECM photography

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Abstract

A novel strategy for imaging commercial black-and-white negative photo films by scanning electrochemical microscopy (SECM) is demonstrated. The imaging is based on using IrCl_6^{3-} as the redox mediator to dissolve silver grains. The SECM probe is biased at a sufficient constant anodic potential (0.8 V vs. Ag QRE) to oxidize IrCl_6^{3-} under diffusion control. SECM images of a patterned band array (2.8 mm \times 3 mm) and of an “EPFL” logo (8.6 mm \times 7 mm) have been recorded with a high resolution from the black-and-white negative photo films. The factors relevant to the quality of images are discussed.

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1. Introduction

Silver halide photography was pioneered in 1839 in France when Jacques Daguerre invented the daguerreotype using a thin-layer of silver iodide as a photosensitive material [1]. Since then, silver halide photography has made remarkable progresses with exposure time decreasing by five orders of magnitude [2–6]. Silver halide crystals are simply produced by mixing solutions of silver nitrate and halide salts (chloride, bromide, and iodide), resulting in a range of crystal shapes and sizes. For the purpose of producing a photographic film, these crystals are distributed in gelatin to make a mixture called the photographic emulsion, which is applied as a thin layer on a polymer support. Upon exposure to light, an electron–hole pair is created in a silver halide grain leading to the formation of a silver atom and subsequently the formation and growth of a silver cluster. The sensitivity of a photographic film stems from the fact that few photons are required to produce a silver cluster in a grain thereby forming the latent image (the state where the recorded image is present on the film

but not yet visible). After processing with a developing agent that reduces all the remaining silver ions of an exposed grain into silver metal, an image becomes visible. The silver halide grains that were not illuminated and were therefore not reduced by the developer are removed by dissolution using the fixer. After development and fixing, the film shows a permanent negative silver image within the gelatin layer. Then, the negative image can be turned into a positive print. The purpose of this communication is to show that negative films can also be imaged by scanning electrochemical microscopy (SECM), and that the quantitative electrochemical readout of silver particles on a negative film provides a high amplification technique for photon detection, which could be used for the design of luminescent sensors.

SECM has successfully grown to be a powerful tool for direct imaging reaction rates on substrate surface [7–13]. The attractive features of SECM for the study of surface reactions and their kinetics [14–17], for high-resolution imaging of chemical or biochemical reactivity on various material surfaces and biological systems [18–29], and for microfabrication [30,31], have been well established in the past two decades. In SECM experiments, the probe is brought to the vicinity of the substrate surface, where the electrochemical response of the probe is recorded as a

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function of the lateral probe position (x, y) for imaging. In comparison with other scanning probe microscopic techniques, SECM possesses some unique features. For example, it is capable of imaging chemical reactivity present at a substrate surface, and samples with relative large surface areas (a few cm^2) and it also has a well-developed quantitative theory.

Recently, we have shown that SECM could be used to image silver or copper stained proteins immobilized on the substrate surface [32–34]. These reports demonstrated the feasibility of using SECM to detect metallic nanoparticles on a porous membrane surface. Then, we applied this technique as a highly sensitive tool for imaging protein-modified latent fingerprints on a poly(vinylidene difluoride) (PVDF) membrane and fingerprints on glass enhanced by a multi-metal-deposition (MMD) approach [35,36]. This methodology takes advantage of the high sensitivity of SECM toward the small variation of electrochemical properties at the substrate surface. Here, we first demonstrate that SECM can also be applied to image quantitatively commercial black-and-white negative photo films with a high quality.

2. Experimental

2.1. Chemicals and materials

Potassium hexachloroiridate (III) (K_3IrCl_6 , Aldrich) and potassium nitrate (KNO_3 , >99%, Fluka) were used as received. Water was deionized to a conductivity of $18.2 \mu\text{S cm}^{-1}$ using a Milli Q plus 185 from Millipore. Alumina $1 \mu\text{m}$, 0.3 and $0.05 \mu\text{m}$, and Mastertex polishing cloths from Buehler were employed to polish the Pt microelectrode. All the black-and-white negative films (Ilford FP4 Plus, 125 ISO and Kodak TMAX, 100 ISO) were shot and processed by the EPFL photographic service (Alain Herzog, EPFL) according to the film manufacturer recommendation.

2.2. SECM measurements

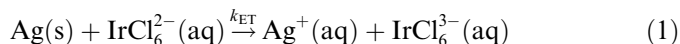
A typical three-electrode setup was employed with a $20 \mu\text{m}$ diameter Pt microelectrode as an amperometric SECM probe. The counter and quasi-reference electrodes are a Pt wire and a silver wire, respectively. The negative film was fixed on a microscope glass slide. This cell assembly was secured onto a platform which includes three screws for leveling the substrate surface. The RG value of the probe ($\text{RG} = R_g/a$, where R_g is the radius of the insulating glass) is about 4. Feedback images of negative films were performed in K_3IrCl_6 (0.1 M KNO_3) solution at a probe potential of $E_{\text{probe}} = 0.8 \text{ V}$ (vs. Ag QRE) while the sample was at open circuit potential (OCP) with a probe-substrate distance ~ 5 or $6 \mu\text{m}$. All of the SECM experiments were carried out with a setup assembled by Gunther Wittstock (University of Oldenburg, Germany) and the image data was treated by using MIRA software [37].

2.3. Optical and electron microscopic imaging

An optical microscope (Axiovert 200, Carl Zeiss, Germany) and a flatbed laser-scanner (HP Scanjet 4890) were used for optical imaging the negative photo films. The electron microscopic imaging was performed on the Philips XL30 FEG field emission scanning electron microscopy with an accelerating voltage of 25 kV .

3. Results and discussion

The imaging is based on the typical amperometric feedback mode, the SECM probe scanning with a constant-height mode over the photo film while simultaneously monitoring the probe current as a function of probe position (x, y). For this purpose, IrCl_6^{3-} is employed as the redox mediator, and the SECM probe is biased at a sufficient constant anodic potential (0.8 V vs. Ag QRE) to oxidize IrCl_6^{3-} under diffusion control. Far from the surface of the photo film, the SECM probe current is limited by the diffusion of IrCl_6^{3-} towards to the probe, leading to a steady-state current (i_{ss}). When the probe is brought close to the relative dark region of the negative-film sample rich in silver clusters, the catalytic recycling of the IrCl_6^{3-} becomes possible according to the following heterogeneous bimolecular electron transfer reaction between IrCl_6^{2-} and metallic silver:



This process leads to an increase in probe current (positive feedback effect). On the other hand, the probe current decreases with the probe approaching the blank substrate due to IrCl_6^{3-} diffusion hindrance (negative feedback effect). Therefore, changes in the probe current during lateral scans used for “chemical imaging” can reflect the picture in the black-and-white negative films.

The feedback effect of SECM can be only observed when the probe is close to the surface usually at a distance less than twice of the probe radius, a . Here, in order to image a relative large area of the negative-film sample with a high resolution, we chose a $20 \mu\text{m}$ diameter probe and the probe-substrate distance was kept at ~ 5 or $6 \mu\text{m}$. The probe-substrate distance was determined by an approach curve carried out on a blank area of the film. To ensure the compatibility of the system with large surface scanning, a scan rate of $100 \mu\text{m s}^{-1}$ is employed. In addition, before SECM imaging, the sample surface was leveled manually as described in the previous report [35].

An array of black-and-white bands was photographed, and Fig. 1a shows an optical picture of the negative-film substrate before the SECM measurements. Ten black bands with $100 \mu\text{m}$ width appear in the relative white ($150 \mu\text{m}$ band space) background. Fig. 1b displays the corresponding SECM image ($2.8 \text{ mm} \times 3 \text{ mm}$) of this sample. The grey scale observed in the SECM-generated image originates from the difference in the electrochemical

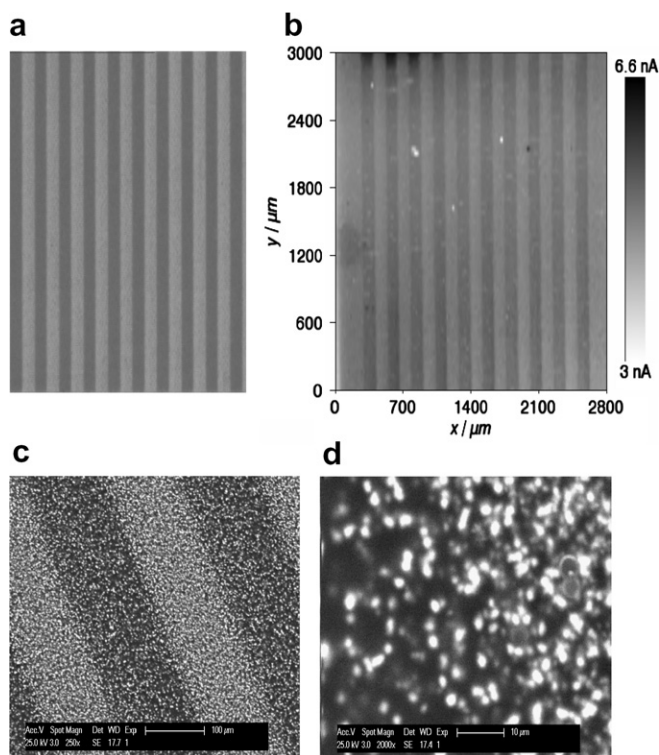


Fig. 1. Images of a black-and-white negative photo film containing a patterned band array obtained by: (a) an optical microscope, (b) SECM (2.8 mm × 3 mm) with 5 mM K_3IrCl_6 (0.1 M KNO_3) and probe-to-substrate distance $\sim 5 \mu\text{m}$, (c) SEM image (250 \times), and (d) high magnification SEM image (2000 \times).

reactivity between black and white bands, as they are covered with different amounts of silver deposits produced during the photographic development process of the negative film. In Fig. 1b, a current density grey scale with current ranging from 3 nA to 6.6 nA is used to illustrate how the probe current changes with the film reactivity. The dark regions in Fig. 1b correspond to the bands where silver halide grains were exposed to light and where therefore silver clusters were formed with a higher density. When imaging the dark regions, the $IrCl_6^{3-}$ consumed at the probe is regenerated by the heterogeneous bimolecular electron transfer reaction (1), and a positive feedback current of 6 nA is thus observed. When imaging the white bands, these contain much fewer silver clusters, so $IrCl_6^{3-}$ is only partially regenerated yielding a low feedback current of 3 nA. The silver clusters density difference between the black and the white bands has also been characterized by SEM. As can be seen from Fig. 1c and 1d, a much higher density of silver clusters appears in the black bands relative to the white ones. In Fig. 1d, the white dots with $\sim 2 \mu\text{m}$ diameter are holes resulting from the dissolution of silver halide grains during the photographic process. In contrast, the white bands contain less silver grains and more white dots. As clearly observed in Fig. 1b, SECM imaging of the black-and-white negative film can differentiate the density of silver grains between the exposed and the non-exposed area providing an image with a good contrast and a high resolution. It should be stressed that the film development was carried out following the film manufac-

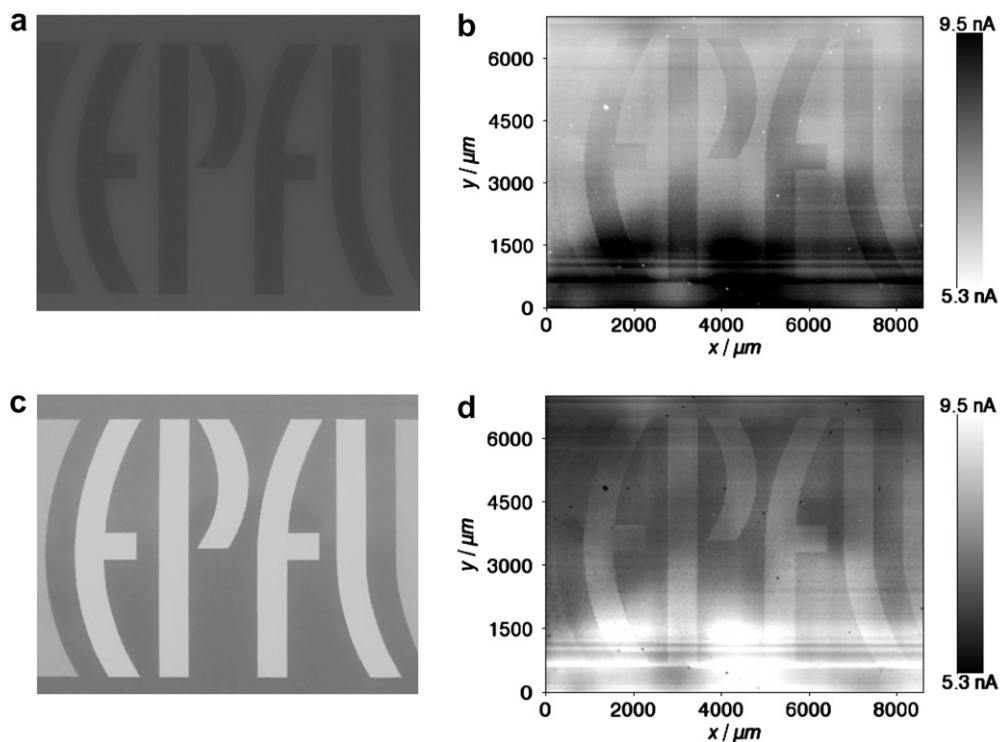


Fig. 2. (a) Image of a black-and-white negative photo film containing “EPFL” logo obtained by an optical laser-scanner, (b) the corresponding SECM image (8.6 mm × 7 mm), (c) after a positive print and then obtained by an optical laser-scanner, and (d) the SECM image (8.6 mm × 7 mm) shown in Fig. 2b but with inverted current density barcode. SECM imaging conditions: 5 mM K_3IrCl_6 (0.1 M KNO_3) and probe-to-substrate distance $\sim 6 \mu\text{m}$.

turer recommendation, and that no silver free area could be obtained.

To further demonstrate the validity of the present SECM methodology, another photo film sample containing the “EPFL” logo was prepared. Fig. 2a shows its image obtained by a flatbed laser-scanner. Displayed in Fig. 2b is a complete SECM image for this logo, which is recorded with a relative large area of $8.6 \text{ mm} \times 7 \text{ mm}$. The logo is clearly resolved with significant positive feedback current on top of a large background current, as the logo letters contain a very high density of silver clusters. Fig. 2c is an optical laser-scanned image of the corresponding positive print of the negative film shown in Fig. 2a. This positive image can also be compared to the SECM image in Fig. 2b by inverting the current density grey scale, as shown in Fig. 2d.

From Figs. 1 and 2, we can see the resolution of the optical graphs is higher than that of SECM images. The major difficulty in the imaging of a photographic film with SECM stems from the presence of the gelatin layer. First, the porous nature of the gelatin hinders the diffusion of the oxidised mediator to the silver grains and that of the reduced mediator back to the probe. Also, the gelatin layer plays the role of a hole trap during the photosensitisation process, which means that it can be oxidised by the oxidised mediator generating a feedback background current. The thickness of black-and-white negative film was determined to be $\sim 30 \mu\text{m}$ by an approach curve measurement carried out on the blank area of negative photo film. As shown in Fig. 3, an approach curve featuring two regimes was recorded. Before point “a” the probe moves close to the film surface and at point “a” touches the surface of gelatin layer, and then penetrates through the whole gelatin layer and arrives at point “b” where touches the surface of the plastic support. Fig. 3 clearly shows that the SECM image illustrated in Figs. 1 and 2 only partially dissolved

the top thin-layer of silver grains as the current increases when the probe scanning over the surface of gelatin layer. Another reason is that we use a relative large electrode located not very close to the gelatin layer in order to avoid probe crash with the rather rough gelatin surface. Thus, the preparation of thinner and smoother films with low background could be useful to improve the quality of SECM photography.

4. Conclusions

It has been shown recently that silver halide photography is a powerful readout tool for an ultrasensitive DNA-detection based as reported by Carell and co-workers [38]. The present SECM methodology can then be used to further amplify this approach. Indeed, it is important to realize that few photons are sufficient to form the latent image on a silver grain, which can be further read out by the SECM re-dissolution of the silver grain using the oxidised mediator. Silver halide films can then be integrated in the design of chemiluminescent sensor where the light generation can be integrated on the film, and then read electrochemically.

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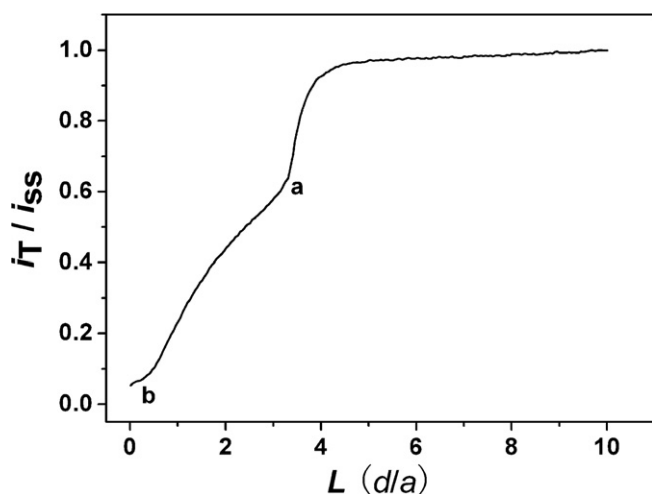


Fig. 3. Approach curve measurement on a blank sample of black-and-white negative photo film. Point a: probe touching the gelatin layer; Point b: probe touching the plastic supporting substrate. Measuring conditions: $1 \text{ mM K}_3\text{IrCl}_6$ (0.1 M KNO_3) and approaching speed $2 \mu\text{m s}^{-1}$.

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