Research Systems, RGA 300). RAIRS spectra were collected with a Nicolet Nexus 670 spectrometer. The polymerization reaction was initiated by a HgXe arc lamp (Oriel) with light intensities from 40 mW cm^{-2} to 240 mW cm^{-2}, as measured by a Newport 1815-C UV power meter. The film thickness was measured using a Tencor Alpha-Step 200 Profiler profilometer and a Rudolph Auto EL II A 9819 ellipsometer operating at 633, 546, and 405 nm. Diffuse reflectance UV-vis spectra were acquired with a Lambda 40 Perkin Elmer UV-vis spectrometer. Film patterning was made possible by inserting a 750-mesh nickel grid immediately before the substrate as a photomask to perform selective polymerization. The resistance of the polypyrrole films was measured with a Keithley 175 A multimeter. To ensure good contact between the probe and the film, the polymer film was coated with a layer of silver paint (SPI).

Received: May 2, 2002
Final version: June 10, 2002

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Redox-Switching of Electrorefractive, Electrochromic, and Conductivity Functions of Cu^{2+}/Polyacrylic Acid Films Associated with Electrodes**

By *Vladimir I. Chegel*, *Oleg A. Raitman*, *Oleg Lioubashevski*, *Yuriy Shirshov*, *Eugenii Katz*, and *Itamar Willner**

Functional polymers of controlled refractivity,[1,2] photochromic,[3,4] electrochromic,[5–7] and optoelectronic[8,9] functions have attracted substantial research activities recently. The use of polymers with tunable refractive properties as optical modulators, optical filters, or electro-optic guided wave devices has been reported.[10,11] Similarly, polymers exhibiting photorefractive properties have been extensively used for optical storage.[12,13] Photochromic and electrochromic polymers have been suggested as active materials for the development of smart windows[14,15] and conductive polymers have been extensively employed as active components in electrically induced light-emitting devices (LEDs).[8,9]

Recently, efforts have been directed toward the development of functional metal or semiconductor nanoparticle–polymer hybrid systems exhibiting tailored sensoric,[16–18] electronic,[19,20] and photoelectrochemical functions.[21,22] Here, we report on the assembly of a redox-switchable Cu^{2+}-ion/polyacrylic acid composite that undergoes electrochemical reduction to a Cu^{0}-nanoparticle/polyacrylic acid composite. We apply surface plasmon resonance (SPR) spectroscopy, absorption spectroscopy, and conductivity measurements to examine the reversible redox switching of the electrorefractive, electrochromic, and conductivity functions of the hybrid polymer. Previous studies have reported on the chemical preparation of Cu-nanoparticle/polymer hybrid systems.[23] Also the reversible electrochemical deposition of metals,[24] e.g., Pb or Cu, on conductive glass as a photochromic layer has been examined. The present study represents a novel Cu^{2+}/polyacrylic acid hybrid system of redox-switchable optoelectronic features.

A polyacrylic acid (PAA) film was electropolymerized on a Au-coated glass plate[25–27] and the film was saturated with Cu^{2+} ions. We used SPR to obtain the thickness and refractive index of the film. Values of the polymer film thickness, d, and complex refractive index, n, obtained by fitting the SPR curve, were $d \sim 280$ nm and $n = 1.372 + 0.02i$. Figure 1 shows the cyclic voltammogram of the resulting Cu^{2+}/PAA film using 0.1 M tris-buffer, pH 5.5, as the electrolyte solution. This cyclic vol-

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[**] The authors gratefully acknowledge the support of the US–Israel Binational Science Foundation.

0935-9648/02/2111-1549 $ 17.50+.50/0

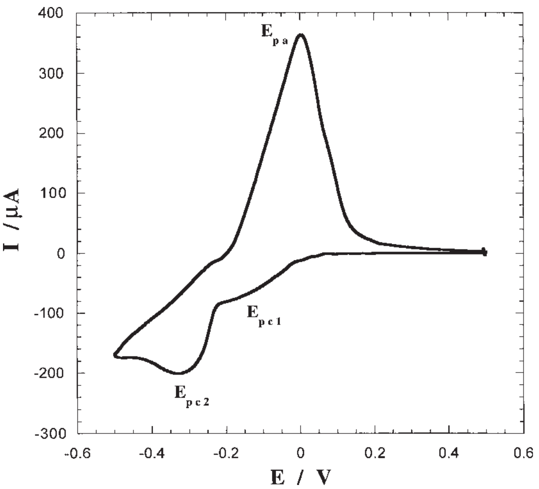

Fig. 1. Cyclic voltammogram of the Cu^{2+}/PAA-modified Au electrode. The data were recorded in 0.1 M tris-buffer, pH 5.5, under argon, potential scan rate 3 $mV\,s^{-1}$.

tammogram follows the known mechanism for the electrodeposition of copper on a Au electrode.[28] Upon sweeping the potential from +0.5 V to –0.5 V a poorly resolved cathodic wave, corresponding to the reduction of Cu^{2+} to Cu^{+}, is observed at $E_{pc1} = -0.12$ V, followed by the reduction wave of Cu^{+} to Cu^{0} at $E_{pc2} = -0.31$ V. Upon sweeping the potential from –0.5 V to +0.5 V the reverse anodic wave is observed at $E_{pa} = 0.0$ V, corresponding to the oxidation of Cu^{0} to Cu^{2+}. It should be noted that the Cu^{+}/PAA state is poorly resolved since it undergoes disproportionation.[28] By coulometric assay of the waves corresponding to the oxidation of Cu^{0} to Cu^{2+}, and assuming that all Cu^{0} is oxidized to Cu^{2+}, we estimate the Cu^{0} content in the film to be ca. 6.3×10^{-8} $mol\,cm^{-2}$.

We followed the redox transitions Cu^{2+}/PAA to Cu^{0}/PAA and back by in-situ electrochemical/SPR measurements. Figure 2A shows the time-dependent SPR curves of the film upon switching the electrode potential from +0.5 V to –0.5 V. The reduction of Cu^{2+} to Cu^{0} metallic nanoparticles is accompanied by a minor change in the position of the SPR minimum reflectivity angle (from 67.3° to 67.7°), but by a substantial increase in the film reflectance and the formation of shallow SPR curves, which become shallower as the Cu^{0} nanoparticles accumulate in the film. We performed a fitting of the SPR reflectance curve corresponding to the Cu^{2+}/PAA film, Figure 2A, curve a. The results indicate no significant difference in film thickness in comparison with the PAA film without Cu^{2+}, and a complex refractive index of the film, $n = 1.374 + 0.007i$. Fitting of the data obtained upon electrochemical formation of the Cu^{0} nanoparticles in the film reveals that the real component of the refractive index of the film, n_{re} is almost unaltered, while the imaginary part of the refractive index, n_{im}, is significantly increased. For example, fitting of the SPR curve obtained after 210 s of Cu^{0} accumulation, Figure 2A, curve h, reveals no significant change in film thickness and a complex refractive index of the film, $n = 1.360 + 0.126i$. The complex dielectric constant of the film, ε, could be calculated from the obtained values of the complex refractive index,[29] using Equations 1 and 2, where Re and Im are notations for the real and imaginary parts of the corresponding value, respectively.

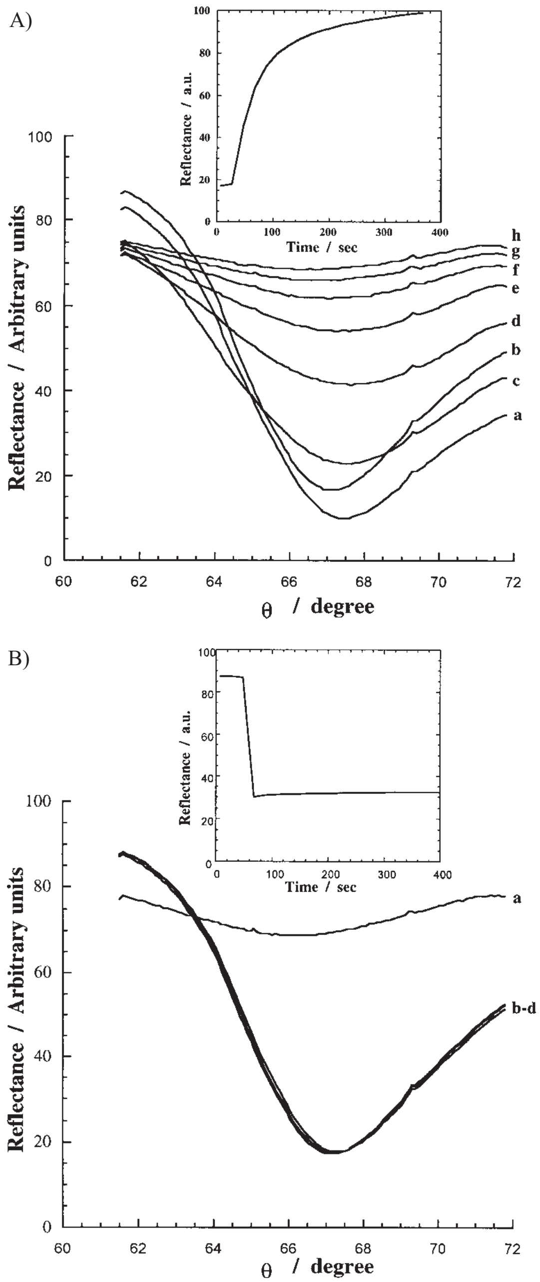

Fig. 2. A) SPR reflectance curves of the Cu^{2+}/PAA-modified Au electrode recorded after the application of a potential step from 0.5 V to –0.5 V: a) 0 s, b) 30 s, c) 60 s, d) 90 s, e) 120 s, f) 150 s, g) 180 s, h) 210 s. Inset: Time-dependent reflectance changes recorded at a fixed angle of incidence ($\theta = 66°$) immediately after application of the potential step from 0.5 V to –0.5 V. B) SPR reflectance curves of the Cu^{0}/PAA-modified Au electrode recorded after the application of a potential step from –0.5 V to 0.5 V: a) 0 s, b) 30 s, c) 60 s, d) 90 s. Inset: Time-dependent reflectance changes recorded at a fixed angle of incidence ($\theta = 66°$) immediately after the application of the potential step from –0.5 V to 0.5 V. All SPR measurements were performed in 0.1 M tris-buffer, pH 5.5.

$$\varepsilon_{Re} = n_{Re}^{2} - n_{Im}^{2} \qquad (1)$$

$$\varepsilon_{Im} = 2\,n_{Re}\,n_{Im} \qquad (2)$$

where $n = n_{Re} + in_{Im}$ and $\varepsilon = \varepsilon_{Re} + i\varepsilon_{Im}$.

The electrochemically induced change in the refractive index implies that the complex dielectric constant ε of the film also alters upon reduction of the Cu^{2+} ions to metallic particles. We found that the dielectric constant of the Cu^{2+}/PAA film is $\varepsilon = 1.89 + 0.02i$, whereas the dielectric constant of Cu^0/PAA is $\varepsilon = 1.83 + 0.34i$. Clearly, the real part of the dielectric constant is almost unaltered, while the imaginary one changes significantly.

At optical frequencies, the complex dielectric constant, ε, is related directly to the metallic conductivity of the material. For light of wavelength λ incident on a material with conductivity σ, the imaginary part of the dielectric constant can be expressed by Equation 3, where c is the speed of light.[29]

$$\varepsilon_{\mathrm{Im}} = 2\sigma\lambda / c \qquad (3)$$

From the optical constants,[30] and using Equation 3, an effective *in-plane* conductivity of Cu^0/PAA corresponding to 8.5×10^3 S m^{-1} is calculated. Thus, the major changes in the complex refractive index of the film may be attributed to the enhanced conductivity of the film containing Cu^0 particles (for a direct analysis of the redox-activated functions of the film see below). Figure 2A, inset, shows the time-dependent SPR reflectance changes at a fixed incidence angle of $\theta = 66°$ upon transformation of the Cu^{2+}/PAA film to the Cu^0/PAA state. The reduction of Cu^{2+} to Cu^0 particles is a relatively slow process and proceeds for ca. 300 s for complete metallization of the film. This is attributed to the fact that the ions have to migrate through the polymer film and reach the electrode surface in order to be reduced. The Cu^0 metallic particles generated electrochemically at the electrode surface provide further conductive sites for the formation of the Cu^0 particles across the polymeric film. Figure 2B shows the SPR reflectance curves of the Cu^0/PAA film upon application of a potential step from –0.5 V to +0.5 V. The Cu^{2+}/PAA is regenerated as evident by the reflectance curve with a minimum reflectance angle at 67.3°. Figure 2B, inset, shows the time-dependent reflectance changes upon oxidation of the Cu^0/PAA film to the Cu^{2+}/PAA film. In contrast to the slow reduction process, the oxidation of the film is fast and proceeds within ca. 30 s. This is consistent with the fact that the conductive Cu^0 particles are aggregated in a metallic network associated with the electrode, and their oxidation is fast. Figure 3 shows the time-dependent reflectance changes at a fixed angle of $\theta = 66°$ of the bare Au electrode, curve a, the PAA-modified Au surface, curve b, and the Cu^{2+}/PAA-modified electrode, curve c, upon the application of a potential step from –0.5 V to +0.5 V and back. The potential step has a small effect on the reflectance of the bare Au surface and the PAA-modified electrode. However, the changes in the reflectance intensities are of opposite direction to that observed for the Cu^{2+}/PAA film. That is, the reflectance of the bare Au electrode and the PAA-modified electrode shows a small decrease upon the application of a potential of –0.5 V, whereas the reflectance of the Cu^{2+}/PAA-modified electrode displays a large increase upon the application of a potential of –0.5 V, and the formation of the Cu^0/PAA film. The redox switching of the reflectance features of the Cu^{2+}/PAA film are fully reversible, Figure 3, inset. While the increase in reflectance corresponding to the formation of the Cu^0/PAA film is slow, the transformation of the film to the Cu^{2+}/PAA state is fast. Interestingly, we do not observe degradation in the reflectance signals, indicating that there is no leakage of Cu^{2+} ions from the polymer film. Presumably, oxidation of the Cu^0 metallic particles associated with the electrode yields Cu^{2+} ions that are trapped in the PAA network. Thus, SPR analysis of the optical properties of the Cu^{2+}/PAA film reveals the redox-switchable electro-refractive properties of the polymer.

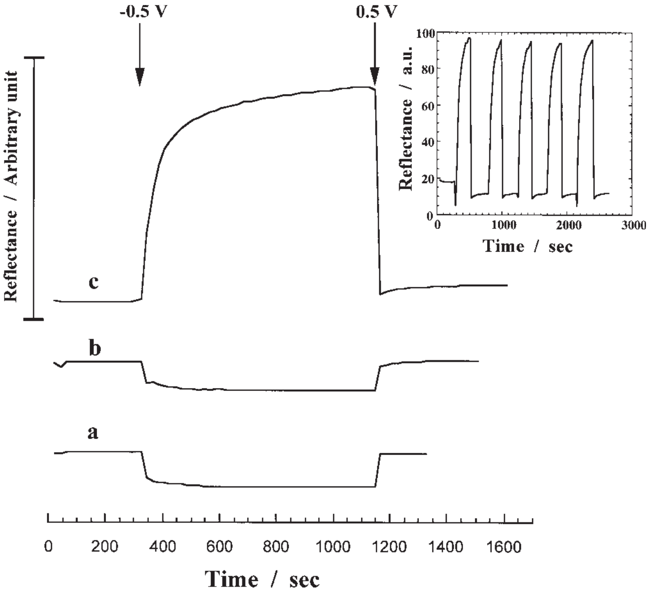

Fig. 3. Time-dependent reflectance changes recorded at a fixed angle of incidence ($\theta = 66°$) upon reversible application of a potential step from 0.5 V to –0.5 V and back from –0.5 V to 0.5 V: a) the bare Au electrode, b) the PAA-modified Au electrode, c) the Cu^{2+}/PAA-modified Au electrode. Arrows show the time when the respective potential was applied. Inset: Time-dependent reversible reflectance changes of the Cu^{2+}/PAA-modified Au electrode recorded at a fixed angle of incidence ($\theta = 66°$) upon multi-potential step switching between 0.5 V and –0.5 V. All SPR measurements were performed in 0.1 M tris-buffer, pH 5.5.

The Cu^{2+}/PAA film associated with the Au-coated glass electrode also reveals redox-switchable electrochromic properties. Figure 4A shows the time-dependent evolution of the absorption features of the film upon the application of a potential step from +0.5 V to –0.5 V on the Cu^{2+}/PAA film. It can be seen that transformation of the Cu^{2+}/PAA film to the Cu^0/PAA state results in an increase in absorbance and in the appearance of an absorbance band with a maximum at ca. 630 nm. This band is attributed to the surface plasmon excitation upon build-up of the Cu^0 nanoparticle network at the electrode support. An enlarged width and red shift of this band relative to the published values[31] of 570–590 nm are probably related to the non-spherical form, coalescence, and interparticle coupling of the Cu^0 particles formed. Figure 4B shows the absorbance changes of the Cu^0/PAA electrode upon switching the potential from –0.5 V to +0.5 V. A fast decrease in the absorbance is observed due to electro-

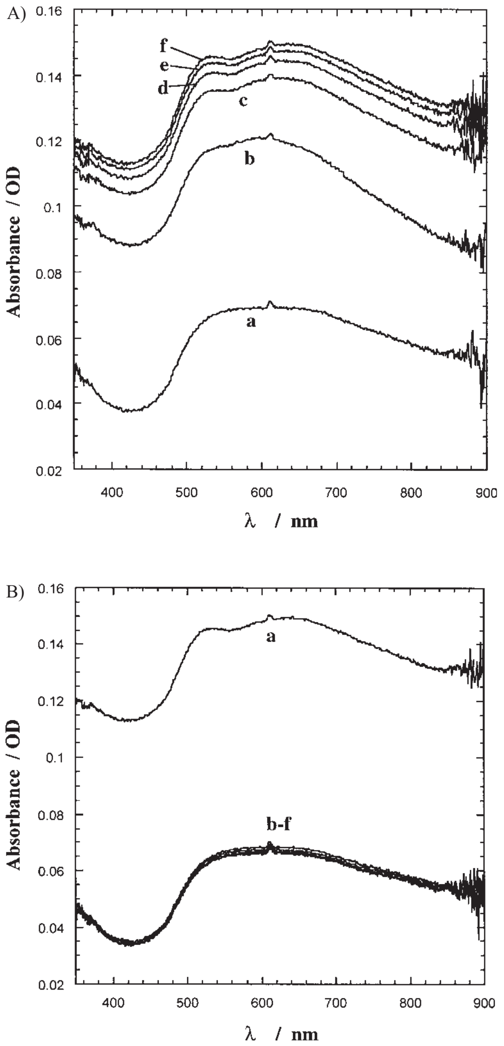

Fig. 4. A) Absorbance spectra of the Cu^{2+}/PAA-modified Au electrode measured after the application of a potential step from 0.5 V to –0.5 V: a) 0 min, b) 1 min, c) 3 min, d) 5 min, e) 7 min, f) 9 min. B) Absorbance spectra of the Cu^0/PAA-modified Au electrode measured after the application of a potential step from –0.5 V to 0.5 V: a) 0 min, b) 1 min, c) 3 min, d) 5 min, e) 7 min, f) 9 min. The spectra were recorded in 0.1 M tris-buffer, pH 5.5, and the spectrum of the bare Au electrode was subtracted from the spectra of the modified electrode.

chemical dissolution of the Cu^0 nanoparticles. The film transmittance changes from 85 % (Cu^{2+}/PAA state) to 70 % (Cu^0/PAA state) at 670 nm. The redox-switchable absorbance changes of the film are reversible, revealing that the Cu^{2+}/Cu^0/PAA system represents a novel electrochromic system.

Analysis of the optical properties of the redox-switchable Cu^{2+}/PAA film reveals that the conductivity features of the film are altered upon redox switching of Cu^{2+}/PAA to the Cu^0/PAA state. We have characterized the transverse (perpendicular) resistivity of the film in its different states by measuring the voltammetric response between the Au-conductive support and a conductive tip (Au wire 0.5 mm diameter) introduced into the polymeric film. A small range (50 mV) potential sweep ($2\ mV\,s^{-1}$) was applied between these two electrodes to measure the conductive properties of the medium under conditions where no electrochemical Faradaic process occurs in the film. Figure 5, curve a, shows the *I–V* curve that corresponds to Cu^{2+}/PAA. From the slope we estimate the film resistance to be ca. 300 kΩ. Reduction of the film to the Cu^0/PAA state followed by measuring the resistance of the film results in the *I–V* curve shown in Figure 5, curve b. The resistance of the film that includes the Cu^0 metallic nanoparticles is substantially lower, $R = 2.2$ kΩ, implying that the film exhibits a significantly higher conductivity. By reversible switching of the film between the Cu^0/PAA and Cu^{2+}/PAA states, the polymer film is cycled between high- and low-conductive states, respectively, Figure 5, inset.

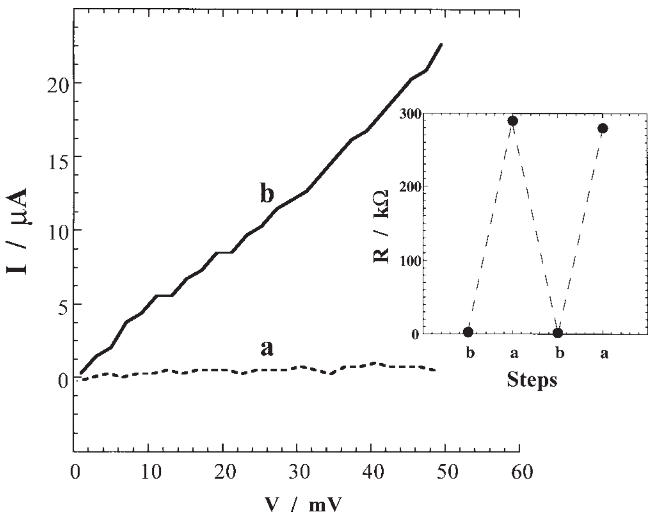

Fig. 5. *I–V* curves of the redox-switched polymer states: a) The Cu^{2+}/PAA-modified Au electrode after application of a potential of 0.5 V. b) The Cu^0/PAA-modified Au electrode after application of a potential of –0.5 V. Inset: Reversible changes of the film resistance extracted from the *I–V* curves upon reversible application of a potential of 0.5 V (steps "a") or –0.5 V (steps "b"). The *I–V* curves were measured between the Au conductive support and a Au wire (0.5 mm diameter) introduced into the polymeric film.

In conclusion, the present study has revealed a new redox-switchable functional polymer consisting of a Cu^{2+}/polyacrylic acid film associated with an electrode support. By redox transformation of the polymer between the Cu^{2+}/PAA and Cu^0/PAA states the electrorefractive, electrochromic, and conductivity properties of the film could be reversibly switched. These electroswitchable properties of the polymer matrix may be used to assemble new types of optical filters,[32] optical modulators,[33] optoelectronic devices,[34] smart windows,[35] and interfaces of controlled conductivity. Preliminary studies indicate that other metal-ion/PAA films such as Pb^{2+}/PAA or Zn^{2+}/PAA show similar redox-switchable optoelectronic properties. The features of these systems will be the subject of a forthcoming report.

Experimental

A surface plasmon resonance (SPR) Kretschmann type spectrophotometer "Biosuplar-2", Analytical-μSystem, Germany (laser diode with wavelength $\lambda = 670$ nm and output power 0.2 mW) was used in this work. The SPR data were processed using "Biosuplar-2" software (version 2.2.30) on a PC computer. The experimental SPR reflectance curves of the polymer film were fitted with the full Fresnel equations in the six-phase model using the Nelder-Mead algorithm of minimization [36]. Cyclic voltammetry and constant potential electrolysis experiments were performed using an electrochemical analyzer (EG&G, VersaStat) linked to a computer (EG&G software #270/250). An open electrochemical cell (230 μL) enabled the easy and rapid removal and exchange of solution above the polymer films. Argon was passed through the funnel placed above the open cell to create an inert atmosphere. Glass supports (TF-1 glass, 20 mm × 20 mm) coated with a Cr sublayer (5 nm) and polycrystalline Au layer (50 nm) supplied by Analytical-μSystem, Germany, were used for the in-situ electrochemical/SPR measurements [37,38]. The Au-coated glass plate was used as a working electrode (1.5 cm^2 area exposed to the solution), an auxiliary Pt and a quasi-reference Ag electrode were made from wires 0.5 mm in diameter and added to the cell. The Ag-quasi-reference electrode was calibrated [39] by referencing to the potential of dimethylviologen, $E^\circ = -0.687$ V vs. SCE, measured by cyclic voltammetry, and the potentials are reported vs. SCE. The SPR-reflectance curves and their time-dependent changes were measured in situ upon application of an external potential to the working electrode.

A polyacrylic acid film was electrochemically produced on the Au-SPR electrode [25–27]. The electropolymerization was performed in an aqueous solution composed of acrylic acid, 2 M, bis-acrylamide, 0.04 M, and $ZnCl_2$, 0.2 M (pH 7.0 adjusted with NaOH). The electrode was preconditioned at the potential of –1.5 V for 10 s, then five potential cycles were applied between –1.5 V and 0.1 V (50 mV s^{-1}) and the cycling was finished at a potential of 0.1 V. The polyacrylic acid modified electrode was treated with HCl, 0.1 M, for 2 min to ensure complete dissolution of Zn^0 produced upon polymerization, the electrode was carefully washed with distilled water to remove excess monomer and Zn^{2+} ions, and subsequently treated with $CuSO_4$ solution, 0.2 M, for 30 min. The $CuSO_4$ solution was removed from the cell and the polymeric film, saturated with Cu^{2+} ions, was washed with water and 0.1 M tris-buffer (tris = tris(hydroxymethyl)aminomethane), pH 5.5, and was added to the cell as electrolyte solution.

The potential-controlled absorption features of the Cu^0/Cu^{2+}/PAA-modified Au electrode were measured with a Uvikon 860 (Kontron) spectrophotometer using a spectroelectrochemical cell composed of a cuvette with the modified working electrode, a Pt counter electrode, and Ag quasi-reference electrode connected to the potentiostat.

Received: May 10, 2002
Final version: August 1, 2002

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Approaching Nanoxerography: The Use of Electrostatic Forces to Position Nanoparticles with 100 nm Scale Resolution

By *Heiko O. Jacobs*,* *Stephen A. Campbell*, and *Michael G. Steward*

This article reports the directed parallel self-assembly of nanoparticles onto charged surface areas. The charged surface areas were fabricated using a parallel method that employs a flexible, electrically conductive, stamp. The conductive stamp was brought into contact with an 80 nm thick film of poly(methylmethacrylate) (PMMA) supported on n-doped silicon. A voltage pulse between the stamp and the silicon was used to pattern charge in the PMMA thin film electret. Areas as large as 1 cm^2 were patterned with charge at a resolution better than 150 nm in 10 s. These charge patterns attract nanoparticles. The directed self-assembly of nanoparticles from a powder, gas phase (aerosol), and liquid phase (suspension) onto high-resolution charge patterns is demonstrated. The accomplished resolution is 800 nm, which is two orders of magnitude higher than what is achieved by today's xerographic printers.

Nanoparticles can provide a variety of functions and are considered as building blocks of future nanotechnological de-

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0935-9648/02/2111-1553 $ 17.50+.50/0