Photolithographically defined Electropolymerized Films. Fabrication of an Electrochemically Switchable Diffraction Grating comprised of *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$

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A combination of photolithography and electropolymerization is utilized to fabricate spatially patterned films of poly-$(bpy)_2Ru(vpy)_2{}^{2+}$; the method has been applied to fabricate *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$ based diffraction gratings.

Incorporation of redox active monomers into spatially patterned arrays and assemblies for utilization as molecular electronic devices is a rapidly growing and challenging area of research.[1,2] Electropolymerization of redox active species on microelectrodes affords a method of producing polymer films that display many interesting and potentially useful properties such as ionic and/or electronic conductivity and electrochromism. However, electropolymerization does not afford a direct means for production of polymer films that are patterned in two dimensions, and only a few reports have appeared which describe approaches to fabricate spatially patterned redox active films.[3] We recently reported a photolithographic scheme that allows preparation of spatially patterned photopolymer films that are electroactive.[4,5] The photolithographic technique affords very good spatial resolution ($\geqslant 5$ µm linewidths), but the photopolymer films display only marginal stability, and comparatively poor electrochemical response. Herein, we report an improved method for fabrication of spatially patterned electroactive polymer films, which combines advantages of photolithography and electropolymerization to afford films that display excellent stability and electrochemical response.

Fig. 1 provides an outline of the photolithography–electropolymerization (PL–EP) method utilized to fabricate microstructured electroactive films.[6] The method employs *poly*-methylphenylsilane (*p*-MPS) as a positive tone photoresist[7] and In–SnO_2 (ITO) coated glass substrates. *p*-MPS is well suited for this application because the polymer is very soluble in non-polar solvents (*e.g.* hexane, toluene) and relatively insoluble in polar solvents (*e.g.* MeCN, DMF, H_2O).[6,7] The versatility and usefulness of *p*-MPS lies in the fact that the near-UV irradiated polymer is easily soluble in moderately polar solvents and can be selectively dissolved exposing the bare electrode surface, while the unirradiated polymer is insoluble in the polar solvents typically used for electrochemistry. This feature allows virtually any monomer that can be electropolymerized to be lithographically patterned onto an electrode using *p*-MPS. For example, Tachibana,[6] *et al.* recently applied *p*-MPS to produce lithographically patterned films of polythiophene by electropolymerization from propylene carbonate. We have used the method to produce patterned films of polypyrrole *via* electropolymerization from aqueous solution[8] and *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$ (bpy = 2,2′ = bipyridine and vpy = 4-vinylpyridine) *via* electropolymerization from MeCN. This communication provides details concerning the *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$ system and the application of the PL–EP method to produce *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$ based diffraction gratings which can be electrochemically switched.

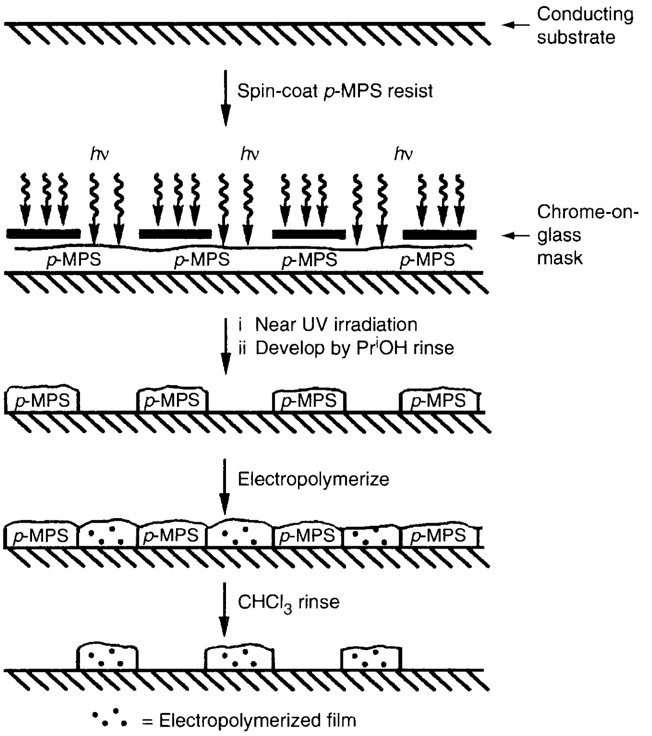

Fig. 1 Schematic diagram of PL–EP technique

In a typical film preparation, a 0.1 mg μl^{-1} p-MPS–toluene solution is spin-coated onto ITO coated glass for 15 s at 4500 rpm.‡ The film is then exposed to near-UV light (366 nm, 60 mW cm^{-2}) for 10–15 min through a Ronchi grating patterned chrome-on-glass mask which has a spatial frequency of 100 lines mm^{-1}. Following light exposure, the film is developed in isopropyl alcohol and dried with N_2. Electropolymerization of $(bpy)_2Ru(vpy)_2{}^{2+}$ is effected by placing a MeCN solution containing 2.5 mmol $[(bpy)_2Ru(vpy)_2][PF_6]_2$ and 0.1 mol tetrabutylammonium hexafluorophosphate (TBAH) into a Teflon electrochemical cell. The ITO substrate which is coated with the patterned p-MPS film is then affixed as the working electrode (WE), the cell is purged with Ar and the WE is cycled three to six times from −0.7 to −2.0 V at a 100 mV s^{-1} scan rate.§ After the cathodic cycling, the *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$ coated electrode is immersed in $CHCl_3$, which dissolves away residual *p*-MPS. Fig. 2 illustrates an optical microscope image of a grating patterned film of *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$ fabricated by this technique.

An anodic CV of a grating patterned film of *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$ on ITO in fresh 0.1 mol dm^{-3} TBAH–MeCN electrolyte exhibits a reversible wave for the $Ru^{II/III}$ couple at $E_{1/2} = +1.38$ V. The $Ru^{II/III}$ wave is very symmetrical and at a 10 mV s^{-1} sweep rate, ΔE_p *ca.* 35 mV. The CV features typical of the patterned *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$ prepared by PL–EP suggest that the charge transport properties of the films are

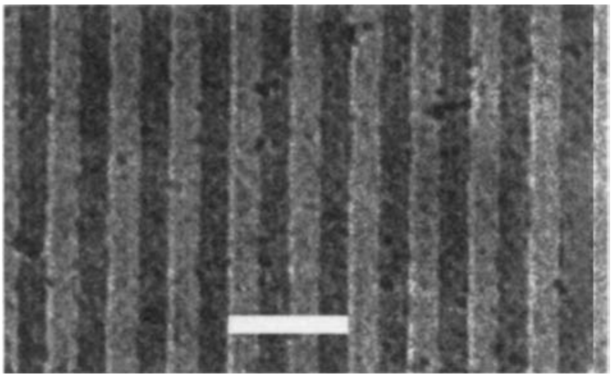

Fig. 2 Transmission optical microscope image of grating patterned *poly*-$(bpy)_2Ru(vpy)_2{}^{2+}$ film on ITO substrate. Darker regions are polymer lines. Horizontal white bar is *ca.* 20 µm.

excellent.[1,10] Integration of the anodic current waves for ten representative PL–EP modified electrodes indicates an average *poly*-$(bpy)_2Ru(vpy)_2^{2+}$ coverage of $\Gamma = 8 \times 10^{-9}$ mol cm^{-2}, while profilometry reveals a typical film thickness of 200 nm.

The grating patterned poly-$(bpy)_2Ru(vpy)_2^{2+}$ films act as phase gratings and diffract light.[11] At resting potential, a typical *poly*-$(bpy)_2Ru(vpy)_2^{2+}$ grating immersed in 0.1 mol dm^{-3} TBAH–MeCN diffracts 650 nm light with a diffraction efficiency (DE)¶ of 0.7%. Furthermore, as demonstrated previously for diffraction gratings comprised of photopolymerized electroactive films, the DE of the *poly*-$(bpy)_2Ru(vpy)_2^{2+}$ grating can be electrochemically switched.[4,5] Fig. 3 illustrates the results of an experiment where the intensity of the first-order diffracted beam from a 650 nm diode laser is monitored while the potential applied to the *poly*-$(bpy)_2Ru(vpy)_2^{2+}$ grating is stepped from +1.0 to +1.6 and then back to +1.0 V. This experiment clearly illustrates that the DE of the *poly*-$(bpy)_2Ru(vpy)_2^{2+}$ grating decreases by approximately 10% when the Ru sites in the film are oxidized to the Ru^{III} state. Furthermore, the DE switching is reproducible with no hysteresis or loss of response for at least 100 cycles. In this regard the *poly*-$(bpy)_2Ru(vpy)_2^{2+}$ diffraction gratings that are fabricated by PL–EP are substantially more stable than the gratings comprised of *photo*polymer films which have been previously reported.

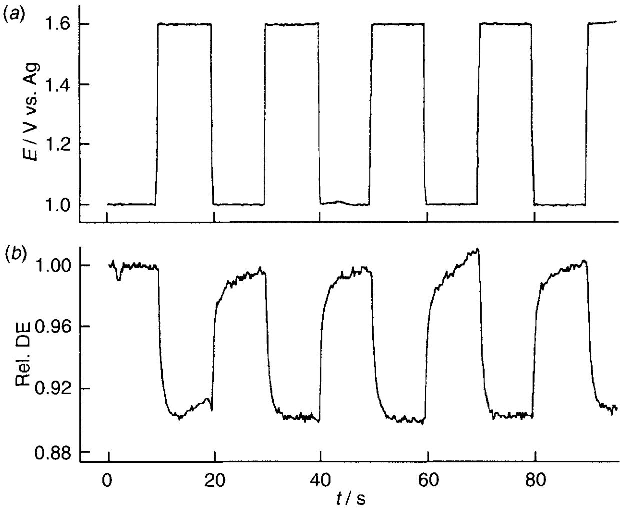

Fig. 3 Effect of electrode potenial on diffraction efficiency of grating patterned *poly*-$(bpy)_2Ru(vpy)_2^{2+}$ film on ITO substrate. (*a*) Potential of working electrode, (*b*) Relative intensity of first-order diffracted beam from a 650 nm diode laser.

In summary, we have developed a new approach to fabrication of electropolymerized films that are patterned on an electrode with a spatial resolution of *ca.* 5 μm. The resulting microstructured films display excellent stability and electrochemical characteristics. Experiments presently underway are exploring the application of PL–EP to fabricate interdigitated diffraction gratings comprised of two or more electroactive species, which can be switched at different electrode potentials.

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Footnotes

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‡ *p*-MPS was synthesized using a literature procedure (ref. 9). GPC indicated a M_w = 2500 g mol^{-1} relative to poly(styrene) standards. ITO coated glass was obtained from Delta Technologies, Stillwater, MN (No. CC-80IN-1509).

§ Potentials reported relative to Ag wire reference (≈ +0.13 V *vs.* SCE).

¶ The DE is defined as the intensity of the first-order diffracted beam divided by the intensity of the undiffracted (zero-order) beam.

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