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Preliminary note

Electrochemical assembly of multicomponent, redox-conductive metallopolymeric films with arbitrary three-dimensional control over macroscopic structure and chemical composition

Hai-Tao Zhang, James C. Bebel and Joseph T. Hupp

Department of Chemistry, Northwestern University, Evanston, IL 60208 (U.S.A.)

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Conducting metallopolymer and, in particular, polymerically-modified electrodes [1] represent an increasingly important area of electrochemical and materials research. Applications now exist in such diverse areas as chemical analysis [2], electrocatalysis [3], photochemical energy conversion [4], display and memory devices [5], and even “molecular electronics” [6]. It has become apparent, however, that in at least some of these areas (most notably, electrochromic devices and energy conversion) further progress may require major new developments in materials fabrication methodologies. In particular there exists a need for new fabrication techniques which can lead, in a controllable fashion, to spatially structured domains and microdomains within polymeric materials. In this note we describe a synthetic approach which leads to multicomponent, multicolor, redox-conductive metallopolymeric films with arbitrary three-dimensional control over structure and chemical composition. (Polymer films featuring arbitrary one-dimensional structuring in the depth dimension have been described previously by Abruña and co-workers [7]. Predefined (i.e. non-arbitrary) two-component structuring in the lateral direction has been described by Kittlesen et al. [8]. Also worth noting are the single-component two-dimensional “pattern generation” experiments of Yoneyama et al. [9] and Okano et al. [10].)

The basis for controlled film assembly in our experiments is electrochemically initiated polymerization [11,12]. Using a semiconductor electrode as the film template, the necessary charges are generated via bandgap excitation [13]. For films prepared in this way, the magnitude of the applied potential and the amount of charge delivered determine the film thickness, while the position and size of the photolysis area define its lateral dimensions. This spatial control combined with the use of multiple materials should permit the assembly of relatively complex, multi-component films.

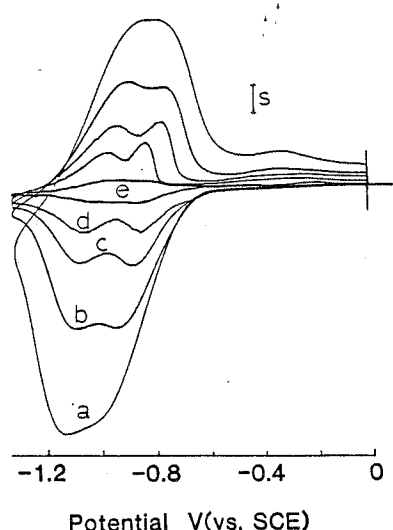


Fig. 1. Cyclic voltammograms of a $\text{Ru}(\text{bpy})_2(\text{vpy})_2^{2+}$ -based polymer film on a p-Si electrode in a 0.1 M tetraethylammonium perchlorate (TEAP) acetonitrile solution under Kr-ion 647 nm (expanded) illumination at (a) 200, (b) 100, (c) 50, (d) 25, (e) 10 mV/s. $S = 100 \mu\text{A}$.

We have tested these concepts using p-type silicon as a template and a krypton-ion laser or mercury-xenon lamp as a photolysis source. ("Monitor quality" boron-doped single-crystal (100) silicon wafers with 1–3 Ω cm resistivity were purchased from Monsanto and sputter-coated with gold to establish backside contact.) For a variety of monomeric vinyl-containing coordination complexes, visibly thick polymeric films have been prepared by photoelectrochemical ligand reduction. Figure 1 shows cyclic voltammetric responses (under illumination) for a representative (unstructured) film based on $\text{Ru}(\text{bpy})_2(\text{vinylpyridine})_2^{2+}$ (bpy is 2,2'-bipyridine). The following are worth noting: (1) The voltammogram shows a linear increase of current with sweep rate (up to 50 mV/s), as expected for a surface-confined redox system. (2) There is a significant photovoltage (ca. 0.5 V). (3) Despite the known extreme photo-lability of pyridyl-based (monodentate) ruthenium systems [14], the film shows excellent electrochemical stability under intense irradiation. The reason, of course, is that the photoeffects are based on bandgap rather than direct molecular excitation.

Figure 2 shows that side-by-side structures of moderate resolution (width $\approx 175 \mu\text{m}$; photolysis spot size $\approx 100 \mu\text{m}$) can be grown from species like $\text{Ru}(\text{vbpy})_3^{2+}$ (vbpy = 4-methyl-4'-vinyl-bipyridine), $\text{Fe}(\text{vbpy})_3^{2+}$ and $\text{Re}(\text{CO})_3(\text{vbpy})(\text{Cl})$. ($[\text{Ru}(\text{vbpy})_3](\text{PF}_6)_2$ [11b], $[\text{Fe}(\text{vbpy})_3](\text{PF}_6)_2$ [11b], $\text{Re}(\text{CO})_3(\text{vbpy})(\text{Cl})$ [3b] and $[\text{Ru}(5\text{-amino-1,10-phenanthroline})_3](\text{PF}_6)_2$ [12a] were prepared and purified by literature methods.) The structures were obtained by successive irradiation in the individual monomer solutions. Figure 3 shows that partial overlayer structures can be fabricated from the same solutions. Depending on the exact photolysis protocol,

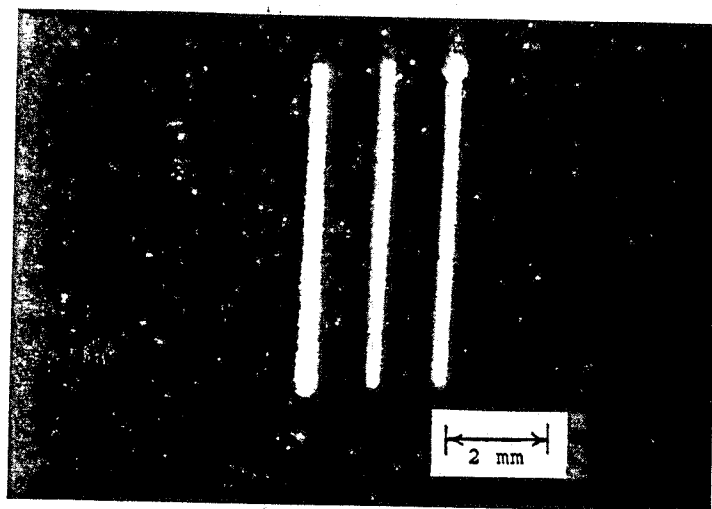


Fig. 2. Side-by-side structures. Left: $\text{Re}(\text{CO})_3(\text{vbpy})(\text{Cl})$ (yellow); center: $\text{Fe}(\text{vbpy})_3^{2+}$ (red); right: $\text{Ru}(\text{vbpy})_3^{2+}$ (orange).

we find that lateral resolution in the overlayer is sometimes compromised if the primary polymer itself behaves as a conduction template (see Fig. 3). More generally, lateral resolution appears to be limited by both polymer growth kinetics and semiconductor (photo-)electrical characteristics; structure widths typically exceed the cross section of the photolysis beam by two- to five-fold. In any case, the

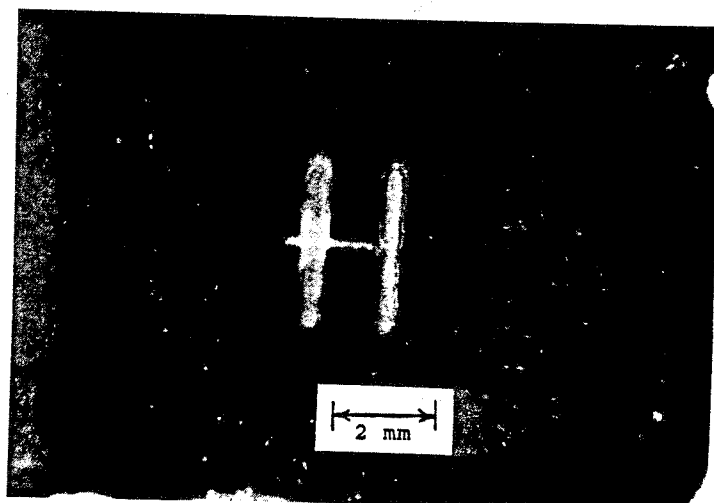


Fig. 3. Two-component polymeric microstructure. The darker lines (red) were grown from $\text{Fe}(\text{vbpy})_3^{2+}$. The lighter line (yellow) is from $\text{Re}(\text{CO})_3(\text{vbpy})(\text{Cl})$.

assembly of both side-by-side (lateral) and overlayer (depth) structures implies the ability (albeit, for a limited number of complexes) to grow metallopolymeric films with arbitrary three-dimensional control over macroscopic structure and chemical composition.

Returning to the problem of lateral resolution, the pertinent (i.e. empirically determined) experimental variables include the monomer concentration, degree of

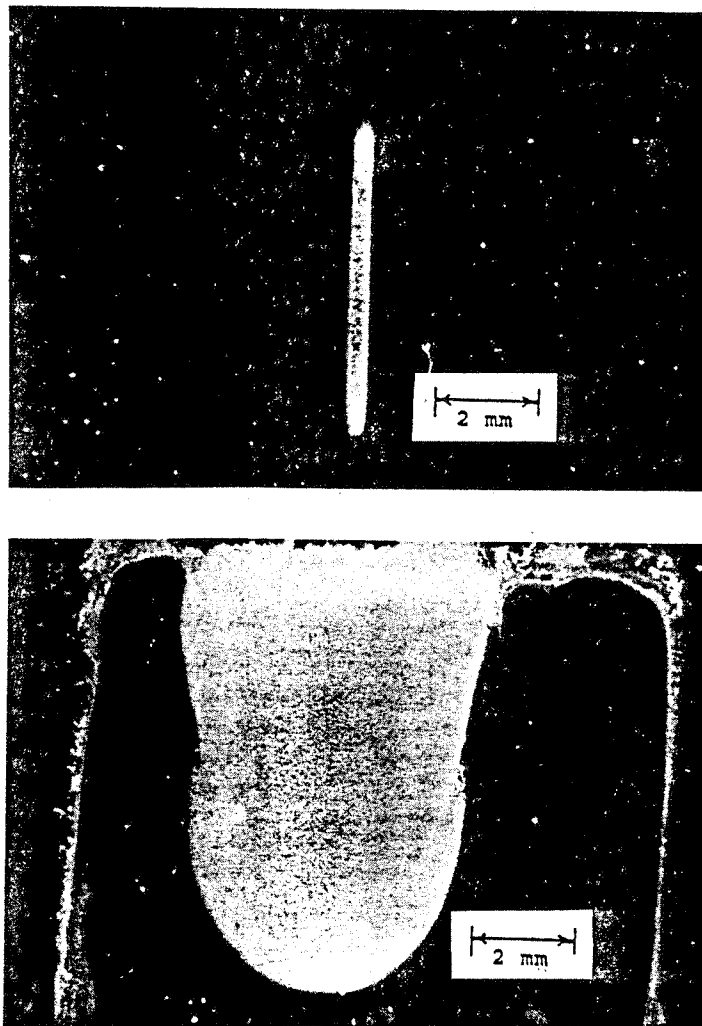


Fig. 4. Dependence of film width on extent of monomer reduction during photolysis (100 μm spot size; ca. 160 $\mu\text{m/s}$ electrode translation rate, 4 translations each direction; Hg-Xe source/blue cutoff filters; p-Si immersed in CH_3CN , 0.1 M TEAP). Upper: photopotential sufficient to reduce only one ligand in $\text{Ru}(\text{vbpy})_3^{2+}$. Lower: photopotential sufficient to reduce two ligands in $\text{Ru}(\text{vbpy})_3^{2+}$.

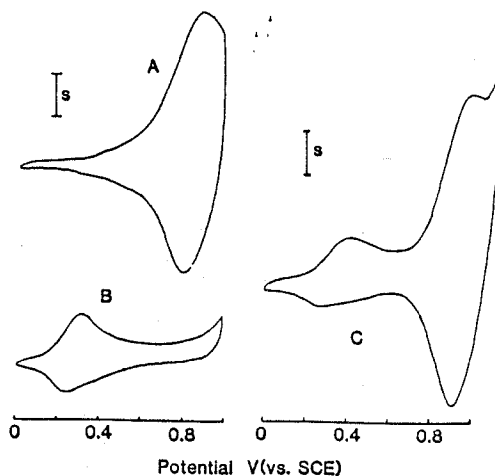


Fig. 5. Cyclic voltammograms of RuL_3^{2+} - and OsL_3^{2+} -based spot films ($\text{L} = 5\text{-amino-1,10-phenanthroline}$) on an n-MoSe_2 electrode in 0.1 M TEAP acetonitrile solution; $S = 20\text{ }\mu\text{A}$, sweep rate = 100 mV/s , light source = Hg-Xe lamp (450 W) with 550 nm cutoff filter. (A) Selective illumination of RuL_3^{2+} -based spot film. (B) Selective illumination of OsL_3^{2+} -based spot film. (C) Entire electrode illuminated.

reduction, electrode (or photolysis beam) translation rate, light intensity, and photolysis spot size. Figure 4 provides a striking illustration of the consequences of manipulating just one of these: the extent of monomer reduction. In the upper panel a film of $200\text{ }\mu\text{m}$ width was obtained by photoelectrochemical reduction of $\text{Ru}(\text{vbpy})_3^{2+}$ to $\text{Ru}(\text{vbpy})(\text{vbpy})_2^+$. In the lower panel, under identical optical and solution conditions, a film of $5000\text{ }\mu\text{m}$ width was obtained via photoelectrochemical creation of $\text{Ru}(\text{vbpy})_2(\text{vbpy})^0$. In essence, in the latter experiment a large insulating surface (dark Si) has been coated electrochemically by lateral propagation from a relatively small conductive region (illuminated Si). Although the detailed mechanistic basis for the lateral spreading effect is not yet completely understood, the available evidence points toward an important role for sustained "dark" free-radical reactivity, presumably by an electrochemically initiated chain-reaction process. It is also possible that enhanced (illuminated) polymer conductivity in the doubly reduced state [6] contributes to the "spreading" effect. In principle, with more appropriate monomers* and templates**, it may be possible to fabricate diffraction-limited structures. Such structures might possibly provide opportunities for unusual electronic device applications [6b]. (See ref. 16 for a discussion as well as proof-of-concept experiments for *organic* conducting polymers.)

* Candidate monomers would include transition-metal complexes of 5-chlorophenanthroline. We have recently shown that these can be electroreductively polymerized by a route that appears to avoid deleterious radical chain-reaction mechanisms [15].

** Because of diminished lateral carrier drift, small grain-size polycrystalline templates might prove more suitable than Si single crystals.

Figure 5 shows that site-selective redox responses can be obtained from appropriate multicomponent structures. The template in this case is n-MoSe₂ (hexagon-shaped single crystals; ca. 7 mm diameter) [17]. An electroactive side-by-side structure was developed by sequential (photo)oxidative electropolymerization [12a] of Ru(5-amino-1,10-phenanthroline)₃²⁺ and Os(5-amino-1,10-phenanthroline)₃²⁺. (The osmium complex was prepared by a method analogous to that for the known ruthenium complex [12a].) Subsequent illumination of the electrode on the poly-osmium side leads to an electrochemical response for Os(III)/(II), while illumination of the poly-ruthenium side leads exclusively to that of Ru(III)/(II). An expanded beam experiment gives the sum of the responses from both sites. The demonstration of site-selective redox chemistry could eventually prove important for advanced electrochromic applications; indeed, we are pursuing such applications. There may also be applications in the general area of electrochemical sensors (especially amperometric sensors) where the availability of light-addressable, multi-functional polymeric devices would be a significant development.

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