

# Deposition of Gradient Materials using Bipolar Electrochemistry

Nafisa Ibrahim

Literature Seminar

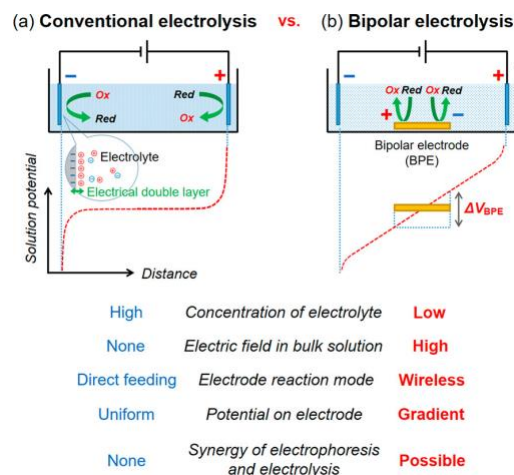
October 15, 2020

The use of electricity to drive synthetic reactions is a sustainable and green approach alternative to hazardous chemical reductants and oxidants.<sup>1</sup> Electron-transfer-based synthesis also offer advantages such as improved reaction selectivity and cost efficiency. In a conventional electrochemical setup, the experiment is performed in a three-electrode configuration consisting of a working electrode, a counter electrode, and a reference electrode where, based on the polarization of the working electrode with respect to the molecules in solution, an oxidation or a reduction reaction occurs at the working electrode (**Figure 1a**).<sup>2</sup> In contrast to conventional electrochemistry, a different configuration conducting electrochemical reactions is bipolar electrochemistry, in which anodic and cathodic reactions occur simultaneously on a wireless conductive electrode in an ionically conducting solution (**Figure 1b**).<sup>1-3</sup> While bipolar electrochemistry has been a subject of interest for scientists for decades, there is a renewed interest with the advent of micro- and nanotechnology due to several notable qualities. The wireless nature of the bipolar electrode (BPE) as well as the unrestricted choices for shape, size, and type of conducting material means that experiments are conducted in the absence of ohmic contact and that if needed, one can have control over hundreds, thousands, and even millions of these electrodes simultaneously.<sup>3,4</sup>

In a conventional electrochemical system, when a sufficiently high voltage is applied between two electrodes in a concentrated supporting electrolyte solution, steep electric fields are generated in the nanometer thick electrical double layer to drive a redox event at the anode and cathode. However, if the supporting electrolyte concentration is low, redox reactions will not occur because the electrical double layer is not formed. This limitation is overcome in a bipolar electrochemical system as the only requirement to drive redox reactions is the sum of the interfacial potential differences ( $\Delta V_{BPE}$ ) at the edges of the BPE to be larger than the potential difference between the target redox reactions. The applied electric field produces a potential distribution across the BPE that depends on the faradaic processes occurring with the highest overpotentials observed at the extremities of the BPE.<sup>5</sup> It

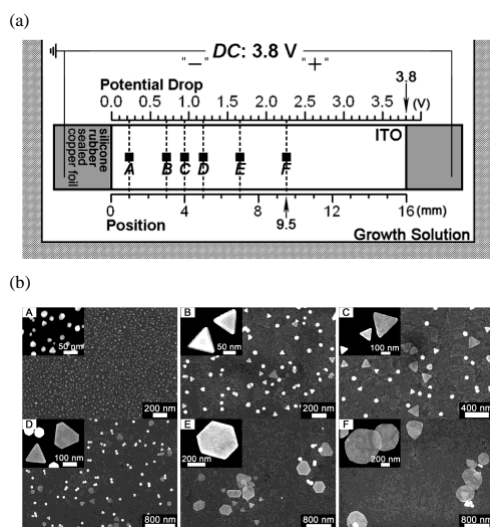
is worth noting that while the generated electric field is depicted linearly (**Figure 1b**), it largely depends on the cell geometry as well the conductivity of the supporting electrolyte.<sup>6</sup> Moreover, in a system with low concentration of supporting electrolyte, the BPE becomes a less resistive path for the current passing through the solution.<sup>7</sup> It is this capacity to generate a wide-range of electric fields that allows scientists to adapt bipolar electrochemistry for a multitude of applications.

BPEs have found applications in sensors, material electrosynthesis, photoelectrodes for solar cells, and electrodeposition of gradient materials and surfaces.<sup>3-4</sup> Gradient surfaces and structures broadly defined are surfaces and structures whose physicochemical properties change gradually over a certain length in space and maybe even in time. Gradient surfaces have an

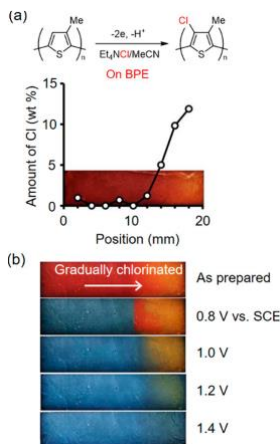


**Figure 1.** Comparison of electrolytic systems for (a) conventional and (b) bipolar electrolysis. Red dotted line represents an ideal electric field generated between driving electrodes.<sup>1</sup>

essential role in high-throughput screening techniques, allowing for fast screening of physicochemical phenomena.<sup>12</sup> Other areas of research on gradient phenomena are the performances of composite and hybrid materials, and the function of advanced electronic materials and devices. Most prominently, natural tissues and organs exhibit an array of spatial gradients. Within the realm of developing biomimetic materials, there is strong efforts to replicate physiological gradients in engineered tissues. Bipolar electrochemistry is a powerful tool for the generation of gradient surfaces as the utilization of anisotropic fields results in gradient distribution of the potential due to the linear drop in IR varied with the applied potential.<sup>7</sup> The ability to generate gradient surfaces is important as gradient surfaces impart variable chemical and physical properties that are especially key in biological systems and sensors.



**Figure 2.** (a) Schematic representation of the experimental setup used to generate a well-defined potential gradient and to synthesize AuNPs. (b) SEM micrographs of AuNPs taken from the positions labeled with corresponding letters A, B, C, D, E, and F in (a).<sup>7</sup>

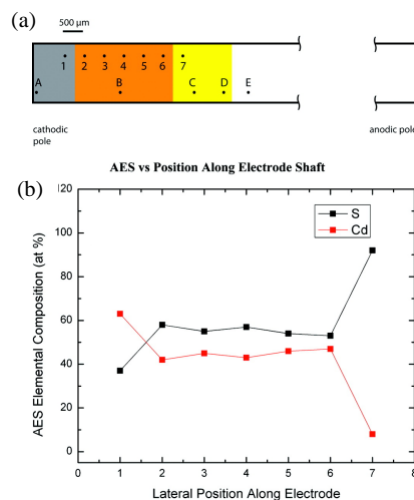


**Figure 4.** (a) Photograph of the gradually chlorinated P3MT film on a BPE and profile showing the amount of chlorine atoms across the film. (b) Photographs of the gradually chlorinated P3MT film during anodic doping at different potentials.<sup>19</sup>

Morphology controlled growth of gold nanoparticles were prepared on a well-defined potential gradient indium tin oxide (ITO) bipolar electrode by Diao et al.<sup>7</sup> Gold triangular nanoprisms and triangular, hexagonal, and polygonal nanoplates were grown with increasing potential of the substrate (**Figure 2b**). The morphology trend was corroborated by performing the experiment in a conventional three-electrode setup signifying the importance of substrate potential for obtaining a wide-range of nanoparticle morphologies. Shape-selective synthesis of nanoparticles on BPE is a facile method that takes advantage of the intrinsic potential gradient induced by bipolar electrochemistry.

One-dimensional chemically compositional gradient solid-state CdS electrodeposited on Au BPE was reported by Shannon et al.<sup>8</sup> The electrodeposition occurred in three distinct regions along the principal axis of

the Au wire which were observed to have different distinct colors based on the species that was deposited (**Figure 3a**). On the cathodic pole of the BPE, Cd-rich CdS deposit had a silver/gray color. Closer to the anodic pole of the BPE, a yellow color was observed due the deposition of elemental S. In the region between the cathodic and anodic poles, CdS deposit had an orange color. These qualitative observations were quantified using Auger electron spectroscopy (AES) in atomic percentage of Cd and S as function of the lateral position along the BPE (**Figure 3b**) providing evidence for the electrodeposition zones observed from the apparent colors on the electrode.

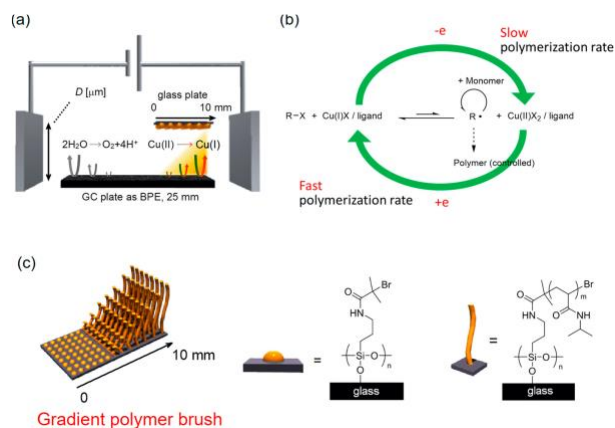


**Figure 3.** (a) Diagram of the geometry used for AES and Raman analysis. (b) Plot of the AES atomic percentage of Cd and S as a function of lateral position along the BPE.<sup>8</sup>

The groups of Fuchigami and Inagi demonstrated gradient patterning of polymeric materials using bipolar electrochemistry. Fuchigami et al. demonstrated electrochemical doping and electrochemical chlorination across conducting poly(3-methylthiophene) (P3MT) films on an ITO bipolar electrode in a U-type electrolytic cell.<sup>9</sup> This was achieved by first doping a neutral PT film on the ITO BPE in non-nucleophilic 5mM Bu<sub>4</sub>NPF<sub>6</sub>/acetonitrile supporting electrolyte solution. Upon passing a constant current through the film in the presence of 5mM Et<sub>4</sub>NCl/acetonitrile supporting electrolyte solution, the color changed in a gradient manner from orange to blue indicative of ionic state formation in the polymer backbone due to the electrochemical chlorination of the film. The amount of doping was quantified by energy-dispersive X-ray (EDX) analysis as a function of the current passed to demonstrate that the degree of chlorination increased linearly with current passage (**Figure 4a**). Gradient chlorination imparts gradient energy across the film as chlorination of the PT film causes resistance to oxidation by lowering the HOMO energy level.

Beyond two-dimensional gradients, three-dimensional gradient poly(*N*-isopropylacrylamide) (NIPAM) brushes were fabricated via electrochemically mediated atom transfer radical polymerization (eATRP) using bipolar electrochemistry by Inagi et al.<sup>10</sup> The potential gradient induced on the BPE allowed for a concentration gradient formation of Cu<sup>I</sup> catalyst by a one-electron reduction of Cu<sup>II</sup>. Since the ratio of [Cu<sup>I</sup>]/[Cu<sup>II</sup>] varied with position on the BPE (**Figure 5c**), the rate of polymerization also varied on the BPE and resulted in a three-dimensional gradient polymerization of NIPAM brushes on a glassy carbon substrate at constant voltage. Infrared reflection absorption spectroscopy (IR-RAS) was used to confirm the formation of poly(NIPAM) brushes. Three-dimensional laser scanning microscope corroborated height profiles that indicated that the film thickness increased on a gradient towards the edge of the BPE cathode. This gradient in the film thickness is a result of the gradient change in the rate of polymerization which is proportional to the ratio of [Cu<sup>I</sup>]/[Cu<sup>II</sup>] along the substrate. Tuning of film thickness was realized by varying the applied voltage,  $\Delta V_{\text{BPE}}$  and the microgap, *D*. The limitation in the range of  $\Delta V_{\text{BPE}}$  to tune film thickness was reached when extremely steep potential gradient led to the two-electron reduction of Cu<sup>II</sup> to generate Cu<sup>0</sup>. Variation in the microgap caused in an exponential increase in the film thickness as the diffusion distance of Cu<sup>I</sup> is proportional to the rate of polymerization. Conclusively, film thickness is easily controlled by varying  $\Delta V_{\text{BPE}}$  and the microgap to generate a wide range of polymer brushes on the substrate.

Various applications of bipolar electrochemistry to fabricate and pattern gradient materials using template-free, simple, and low-cost electrolytic setup was demonstrated by the groups of Diao, Shannon, Fuchigami, and Inagi. Formation and patterning of gradient materials using bipolar electrochemistry is an important novel technique that imparts gradient functionality for various essential applications in biochemical sensing as well as explorations within the realm of materials science and chemistry.



**Figure 5.** (a) Schematic illustration of the setup for surface-initiated eATRP using a BPE system. (b) General scheme for eATRP using a Cu catalyst. (c) Representation of a gradient poly(NIPAM) brush propagated from an initiator-modified glass substrate.<sup>1,10</sup>

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