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Review Article
Bipolar electrochemistry—A wireless approach for electrode reactions

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Bipolar electrochemistry involving two feeder electrodes and a conducting object (the bipolar electrode) in an electrolytic solution has attracted a renewed interest in the last two decades due to its use within several fields ranging from materials science to sensing and beyond. The potential difference between the electrolyte and the bipolar electrode may drive oppositely directed faradaic reactions (reduction/oxidation) at the cathodic and anodic sides of the bipolar electrode. The potential difference between the solution and the bipolar electrode is highest at the extremities, which means that the potential difference for driving the faradaic processes is always largest here. This wireless technique generates an asymmetric reactivity at the surface of a conducting object allowing for modification of more delicate materials such as graphene or for simultaneous modification of an array of electrodes. In this review, the recent applications of bipolar electrochemistry are presented focusing on sensing, electrografting, electrodeposition, and the use of graphene as a bipolar electrode.

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Introduction

Bipolar electrochemistry is a well-established technique, which has been known for many years [1]. In the late 1960s, Fleischmann and co-workers described fluidized bed electrodes, where electrochemical reactions at discrete conductive particles took place, when a voltage was applied between two feeder electrodes [2]. Since these early studies, bipolar fluidized bed electrodes have been applied to improve the efficiency of electrosyntheses [3], photoelectrochemical cells [4], and batteries [5]. Recently, bipolar electrochemistry has attracted renewed interest in fields ranging from site-selective electrodeposition [6] to electrogenerated chemiluminescence (ECL) [7].

Today a bipolar electrode (BE) refers to any conducting object exhibiting oxidation and reduction reactions at the same time, i.e. it acts simultaneously as an anode and a cathode [8]. This is a distinct difference from a standard two- or three-electrode setup, where the cathode and the anode are physically separated. Over the last two decades bipolar electrochemistry has experienced an exponential growth in the number of users. In 2016 an entire issue of *ChemElectroChem* was devoted exclusively to bipolar electrochemistry [9]. Various reviews on bipolar electrochemistry and the underlying principles are already available [1,10]. The objective of this review is, first of all, to give an overview of some of the most recent results obtained within sensing, electrografting, and electrodeposition using bipolar electrochemistry.

Sensing

The basic operating principle of bipolar electrochemistry sensing relies on electrical coupling between the sensing and the reporting poles. This is valid because the rates for the two opposite faradaic processes at the two poles are exactly equal. The magnitude of the current running through a BE can be indirectly determined by ECL as a reporting mechanism. In ECL electrochemically generated intermediates undergo a highly exergonic reaction to produce an electronically excited state, which emits light [11]. A system, which is often applied, is the oxidation of $[Ru(bpy)_3]^{2+}$ in the presence of tripropylamine (TPrA) as a co-reactant, which results in red light emission (see Figure 1). Luminol-based ECL has also been investigated [12], and both luminophores ($[Ru(bpy)_3]^{2+}$ and luminol) were introduced for simultaneous ECL emission at distinct wave lengths resulting in blue and red light, respectively [13]. ECL in combination with bipolar electrochemistry was used to detect cancer biomarkers [14], but also in connection with chemomechanical electrochemiluminescent motion (see Figure 1) [15,16].

Figure 1

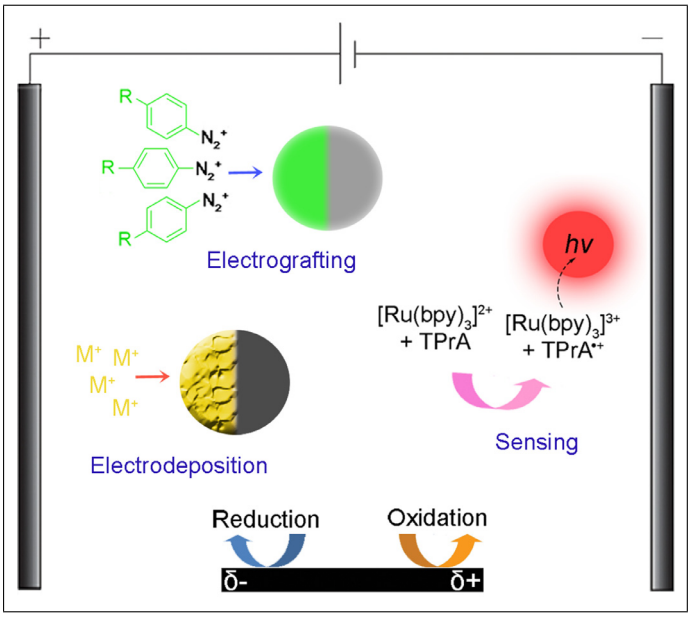

Illustration of a bipolar setup showing at the same time some of the applications of bipolar electrochemistry, i.e. electrografting, electrodeposition, sensing, and electrode processes at graphene.

Recently, ECL was generated from a suspension of multi-walled carbon nanotubes (CNTs), where each tube acted as an individual nano-emitter [17]. Usually, ECL is confined to the electrode surface, but this intrinsic limitation was overcome by generating ECL at nano-emitters in solution. This approach adds a new spatial dimension by switching from a surface-limited process to 3D electrogenerated light emission [17]. In another study, ECL was used for sensing using a closed bipolar cell setup [18]. In addition to ECL, other techniques have been implemented for sensing, including fluorescence [19,20]. Furthermore, vinyl substituted $[Ru(bpy)_3]^{2+}$ was recently copolymerized with *N*-isopropylacrylamide (NIPAM) by indirect reductive polymerization. Afterward ECL/fluorescence microscopy was used to map the polyNIPAM on the BE, and the intensity changes in the ECL was correlated with the swollen/collapsed state of the polyNIPAM [21].

Electrografting

Electrografting of aryldiazonium salts has recently been achieved by bipolar electrochemistry. In 2013 Zigah and co-workers for the first time reported on the bipolar electrografting of aryldiazonium salts, more specifically 4-nitrobenzenediazonium and 4-carboxybenzenediazonium (see Figure 1) on a glassy carbon bead [22••]. This work was further extended to include bipolar electrografting of the inner wall of CNTs [23•]. Bipolar electrografting has also been employed to create initiator films for atom transfer radical polymerization (ATRP). Inagi and co-workers used indium tin oxide (ITO) as BE for the grafting of 4-(2-hydroxyethyl)benzenediazonium [24].

To further expand the use of aryldiazonium salts for bipolar electrografting, we designed a bifunctional aryldiazonium salt for single step double deposition [6]. The novel bipolar electrografting methodology presented uses a single grafting agent, where concomitant deposition of two chemically different organic layers was achieved via simultaneous reductive and oxidative electrografting [6]. Furthermore, it has been shown that it is possible to electrograft not only aryldiazonium salts, but also diaryliodonium and triarylsulfonium salts [25].

Electrodeposition

A common use of bipolar electrochemistry is within the field of electrodeposition and/or electrodissolution of metals and organic molecules. Electrodeposition on BE beads to form asymmetrically modified particles is also possible with this technique due to its inherent wireless property. Reduction of a metal salt on the cathodic side of a bead afforded an asymmetrical modification of the substrate [26]. In a more recent study, particles with sophisticated surface patterns were obtained [27•]. This was further explored for the deposition of inorganic and polymeric layers [28,29] as well as the synthesis and deposition of metal–organic frameworks [30].

Several metal compositional gradients were synthesized by bipolar electrodeposition, including Ni/Cu [31,32], Ni/Mo/Co [33•], and Cu/Ni/Zn [34]. In all cases, the