Bipolar Electrochemistry: From Materials Science and Motion and Beyond

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CONSPECTUS

Bipolar electrochemistry, a phenomenon which generates an asymmetric reactivity on the surface of conductive objects in a wireless manner, is an important concept for many purposes, from analysis to materials science as well as for the generation of motion. Chemists have known the basic concept for a long time, but it has recently attracted additional attention, especially in the context of micro- and nanoscience. In this Account, we introduce the fundamentals of bipolar electrochemistry and illustrate its recent applications, with a particular focus on the fields of materials science and dynamic systems.

Janus particles, named after the Roman god depicted with two faces, are currently in the heart of many original investigations. These objects exhibit different physicochemical properties on two opposite sides. This makes them a unique class of materials, showing interesting features. They have received increasing attention from the materials science community, since they can be used for a large variety of applications, ranging from sensing to photosplitting of water. So far the great majority of methods developed for the generation of Janus particles breaks the symmetry by using interfaces or surfaces. The consequence is often a low time-space yield, which limits their large scale production. In this context, chemists have successfully used bipolar electrodeposition to break the symmetry. This provides a single-step technique for the bulk production of Janus particles with a high control over the deposit structure and morphology, as well as a significantly improved yield. In this context, researchers have used the bipolar electrodeposition of molecular layers, metals, semiconductors, and insulators at one or both reactive poles of bipolar electrodes to generate a wide range of Janus particles with different size, composition and shape.

In using bipolar electrochemistry as a driving force for generating motion, its intrinsic asymmetric reactivity is again the crucial aspect, as there is no directed motion without symmetry breaking. Controlling the motion of objects at the micro- and nanoscale is of primary importance for many potential applications, ranging from medical diagnosis to nanosurgery, and has generated huge interest in the scientific community in recent years. Several original approaches to design micro- and nanomotors have been explored, with propulsion strategies based on chemical fuelling or on external fields. The first strategy is using the asymmetric particles generated by bipolar electrodeposition and employing them directly as micromotors. We have demonstrated this by using the catalytic and magnetic properties of Janus objects. The second strategy is utilizing bipolar electrochemistry as a direct trigger of motion of isotropic particles. We developed mechanisms based on a simultaneous dissolution and deposition, or on a localized asymmetric production of bubbles. We then used these for the translation, the rotation and the levitation of conducting objects. These examples give insight into two interesting fields of applications of the concept of bipolar electrochemistry, and open perspectives for future developments in materials science and for generating motion at different scales.
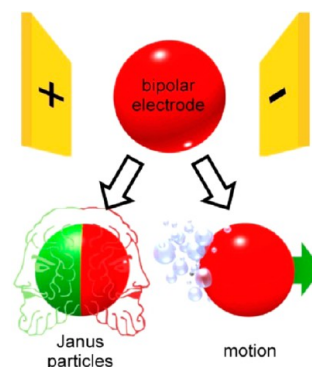
Introduction

In order to understand the basic concept behind bipolar electrochemistry, let us consider the situation depicted in Figure 1a, where a conducting object is immersed in a solution exposed to an external electric field, applied between the electrodes. In the absence of electric field, the immersed conducing object is at a mixed potential E_m. A potential difference is applied between the two electrodes.

E_a and E_c being the potential of the anode and the cathode respectively, L being the distance between the two feeder electrodes, the electric field value $\mathscr{E}$ is given by

$$\mathscr{E} = \frac{E_a - E_c}{L} \qquad (1)$$

if in a first order approximation, the imposed potential drops linearly across the electrolyte solution (blue line in Figure 1a). As a consequence of the presence of the electric
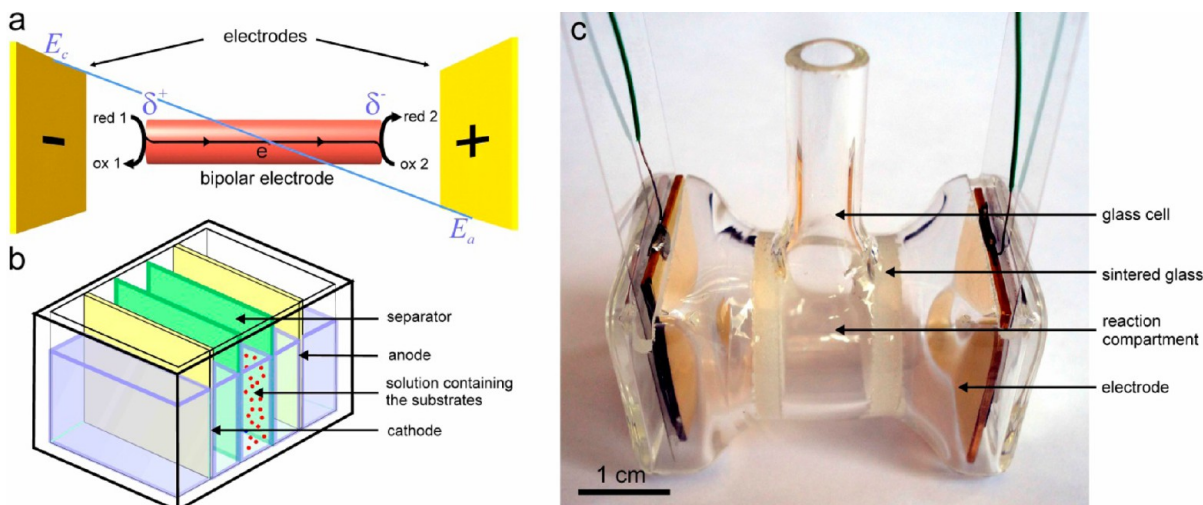
FIGURE 1. Bipolar electrochemistry, principle and devices. (a) Scheme showing the behavior of a cylindrical conducting object, immersed in a solution containing the electroactive species red 1 and ox 2, and exposed to a sufficiently high electric field to promote bipolar electrochemistry. (b) Scheme showing the design of a bipolar electrodeposition cell. (c) Glass cell used for bipolar electrodeposition.

field, a polarization potential E, which is given by the difference of the solution potential value with respect to the conducing object, arises. The value of E varies along the object/solution interface and can be calculated at a position x on the object as

$$E = \mathscr{E}x \quad (2)$$

for a linear object. The maximum polarization potential difference occurs between the extremities of the object, and its value ΔV can be calculated as

$$\Delta V = \mathscr{E}l \quad (3)$$

with l being the characteristic dimension of the conducing object. This value is directly related to the reactivity at the extremities of the polarized interface. In the presence of electroactive species, red 1 and ox 2, which can undergo the following reactions:

$$red1 \rightarrow ox1 + n_1 e^- \quad (4)$$

and

$$ox2 + n_2 e^- \rightarrow red2 \quad (5)$$
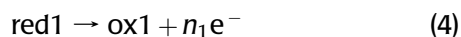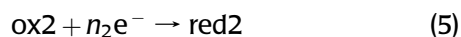
with n_1 and n_2 being the number of electrons involved for each electrochemical reaction and the two redox couples red 1/ox 1 and red 2/ox 2 having a standard potential E_1^0 and E_2^0, respectively. One can assume that the minimum potential value ΔV_{min}, needed to induce reaction 4 and 5 at both sides of the polarized interface, has to be, in a first order approximation, at least equal to the difference of the standard potentials of the two involved redox couples

$$\Delta V_{min} = E_1^0 - E_2^0 \quad (6)$$

If the condition $\Delta V > \Delta V_{min}$ is fulfilled, that is, $\mathscr{E}$ is important enough for a conducting object with a given size (eq 3), electrochemical reactions 4 and 5 can occur simultaneously at both extremities of the object. Because under these conditions the object is behaving at the same time as an anode and a cathode, we refer to it as a bipolar electrode (BPE). The BPE can be any kind of conductive material with any characteristic dimension and geometry. However, as it is stated in eq 3, a smaller object will require a higher external electric field to be sufficiently polarized in order to behave as a BPE. In other words, for a given electric field in the solution, the polarization will be smaller for objects with smaller dimensions, which has a direct influence on the kinetics of the two redox reactions. In the case of electrodeposition processes, this will therefore have also a considerable impact on the morphology of the deposit, ranging from crystalline to amorphous.

The total current flowing through the system is divided into two fractions in the vicinity of the conducting object. The faradaic current flows through the BPE via electronic conduction, whereas the bypass current flows through the solution via migration of charged species. More details about theoretical aspects can be found in the literature.[1,2]

A typical cell used for bipolar electrodeposition on microparticles is presented in Figure 1b and c. In this configuration, the conducting particles and the reactants are placed in the middle compartment, whereas the two side compartments contain the electrodes and a solvent, or a mixture of solvent with a small concentration of electrolyte. Typically tensions
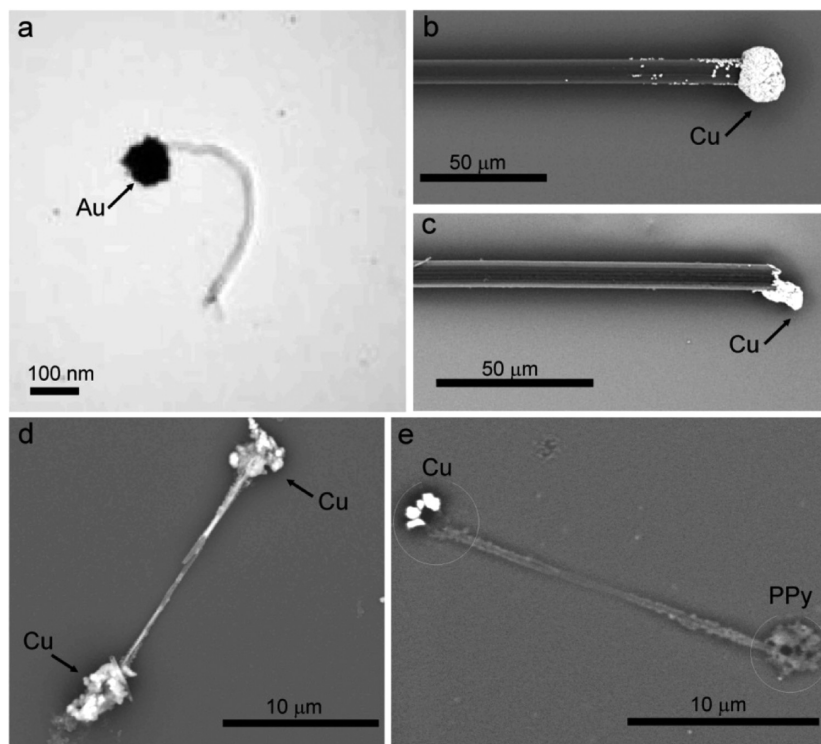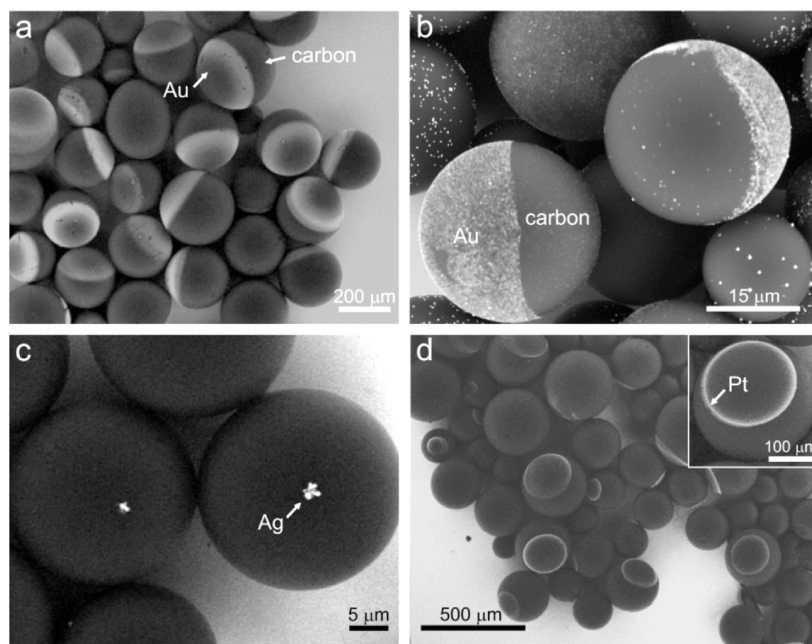
FIGURE 2. Scanning electron micrographs showing carbon substrates modified by bipolar electrodeposition. (a) Multiwall carbon nanotube modified at one extremity with gold. Adapted with permission from ref 30. Copyright 2008 American Chemical Society. (b) Carbon microfiber modified at one extremity with a copper deposit, centered with respect to the tube axis. Adapted with permission from ref 35. Copyright 2012 American Chemical Society. (c) Carbon microfiber modified at one extremity with a copper deposit, noncentered with respect to the tube axis. Adapted with permission from ref 35. Copyright 2012 American Chemical Society. (d) Carbon microtube modified at both extremities with copper deposits. Adapted with permission from ref 33. Copyright 2011 American Chemical Society. (e) Carbon microtube modified at one extremity with a copper deposit and at the other extremity with polypyrrole. Adapted with permission from ref 33. Copyright 2011 American Chemical Society.

of up to several thousand volts are applied between the two electrodes. The separators prevent the particles from being affected by the bubble production that occurs at the electrodes.

Bipolar electrochemistry has been known for quite a long time, and it has been used since the 1970s for designing electrochemical reactors and batteries.[1,2] In the present decade, it has gained considerable additional attention.[3,4] The concept has shown a strong potential for the elaboration of integrated circuits,[5] electrical contacts,[6] and electronic devices.[7] It has also been used for analytical purposes such as preconcentration,[8,9] separation,[10,11] electrochemical sensing,[12,13] and optical detection.[14,15] In the present contribution, our interest will be focused on the applications of bipolar electrochemistry for materials science and for the generation of motion. More than a decade ago, the group of Bradley was the first one to use bipolar electrodeposition for material science, especially in the context of the modification of microobjects,[16] whereas the use of this concept for the propulsion of objects is much more recent. In the following, we will review the latest developments in both fields and emphasize the advantages of these approaches.

Bipolar Electrochemistry in Materials Science

Breaking the symmetry during the synthesis or the modification of materials leads to composition gradients and in the extreme case to completely asymmetric objects. Molecular or material gradients are important for biosensing, spectroscopy, and optics. Various strategies involving, for instance, microfluidic systems[17] or electrochemistry,[18] have been reported for their generation. Asymmetric particles, so-called Janus particles (JPs), are also of great importance for various applications ranging from therapeutics to catalysis.[19] So far the great majority of methods, developed for the generation of JPs, break the symmetry by using interfaces or surfaces. This makes the preparation of large quantities rather difficult, because those techniques usually lead only to single layer equivalents of objects, as the modification occurs in a two-dimensional reaction space.[19] In this context of symmetry breaking, two key features of BPEs are very important: (i) the control of the gradient of polarization potential along the surface of the object and (ii) the intrinsically asymmetric reactivity. This makes bipolar

FIGURE 3. Scanning electron micrographs showing carbon beads modified by bipolar electrodeposition of metals. (a) Submillimetric glassy carbon beads coated with gold. Adapted with permission from ref 31. (b) Micrometric glassy carbon beads coated with gold. (c) Micrometric glassy carbon beads with a localized silver electrodeposit. Adapted with permission from ref 31. (d) Submillimetric glassy carbon beads modified with platinum rings. Inset: zoom on one particle.

electrochemistry an appealing and unique tool for the easy and wireless synthesis of material gradients and JPs.

Materials Modification at the Molecular Level. Ulrich et al. used the gradients of polarization potential at BPEs for creating self-assembled monolayer (SAM) gradients that were postfunctionalized with proteins.[20,21] Millimeter long gold wafers, functionalized with a thiolated polyethylene glycol (PEG) SAM, were used as BPEs. Under the influence of the electric field, the SAM was toposelectively desorbed from the cathodic pole, leading to a molecular gradient at the gold surface. The naked gold surface was then backfilled with another functionalized PEG, which promoted the formation of a lysozyme gradient. It was recently shown that BPEs based on azide-functionalized conducting polymers (CPs) can be gradually modified by "click" chemistry in the presence of Cu^{2+} and an alkyne.[22] The local generation of Cu^+ at the cathodic pole catalyzes the grafting.

Bipolar electroreduction of aryldiazonium salts at the cathodic pole of glassy carbon (GC) BPEs was recently employed for the synthesis of Janus beads, half-covered with molecular layers.[23] In this work, the presence of the grafted organic layers was revealed either by coadsorption of gold nanoparticles or by coupling with a fluorescent probe (Figure 4d). The fine control over the modified area was demonstrated. The possibilities offered in terms of diversity of organic moieties that can be grafted is very promising for applications such as micromotors[24] and sensing.[25]

Metal Deposition. Ramaswamy and Shannon reported the formation of Ag–Au alloy gradients on stainless steel substrates. After the formation of a thiophenol monolayer on the surface,[26] surface enhanced Raman scattering was evaluated along the BPE, revealing its maximum effect for an Ag atom percentage of about 70.[26]

Asymmetric bipolar electrodeposition on microparticles has been first reported by Bradley's group.[16] Their pioneering concept consisted of applying an electric field perpendicular to track etched membranes or cellulose paper with one layer of adsorbed particles. These surfaces are used to ensure the particle immobilization during the bipolar electrodeposition. The first publication reported the modification of micrometer-sized amorphous graphite particles with Pd.[16] In this case, a Pd^{2+} salt was reduced at the cathodic pole and the solvent was oxidized at the anodic pole of the BPEs. The same technique has also been used to create hybrid Au/carbon/Pd micro-objects, by exposing the membranes to two different plating baths for two successive bipolar electrodeposition runs.[16] Pulsed bipolar electrodeposition was performed for depositing Pd onto graphite powders.[27] This team also focused their attention on the modification of anisotropic carbon substrates such as carbon nanofibers, carbon nanotubes and carbon nanopipes.[28,29] A similar setup was used, but, in this case, the cellulose paper was oriented parallel with respect to the electric field.
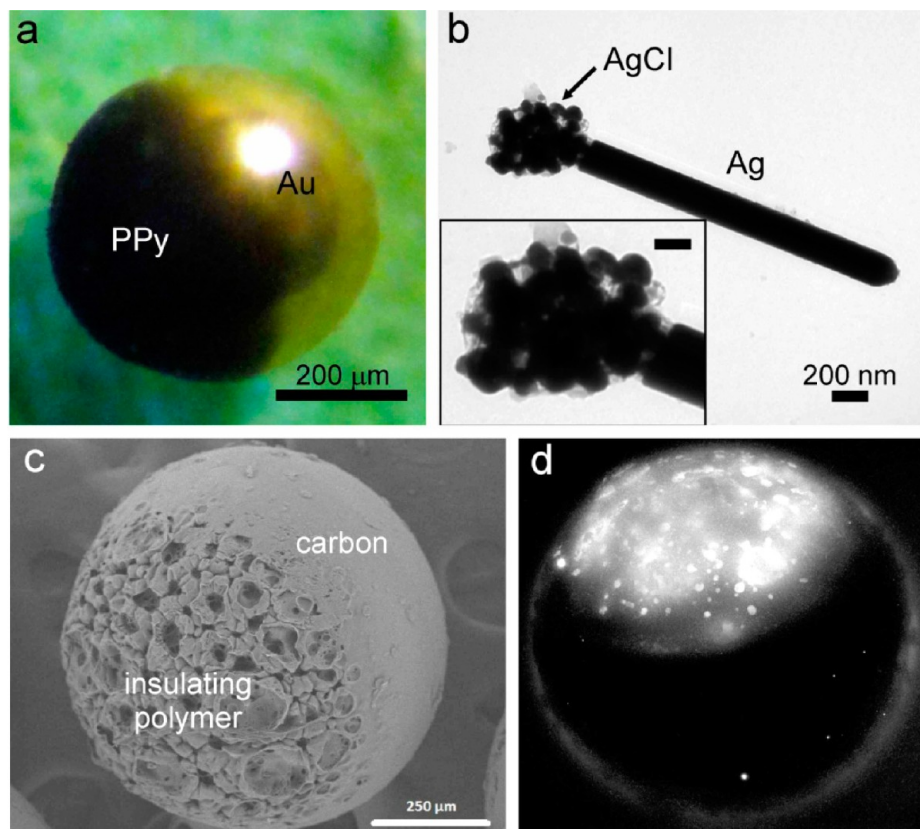
FIGURE 4. Bipolar electrodeposition of nonmetallic materials. (a) Optical micrograph showing a gold bead half-coated with polypyrrole. (b) Transmission electron micrograph showing a silver nanowire modified at one extremity with silver chloride. Inset: detail of the deposit; the scale bar equals 100 nm. Adapted with permission from ref 31. (c) Scanning electron micrograph showing a submillimetric glassy carbon bead modified with an insulating organic polymer. Adapted with permission from ref 41. Copyright 2012 American Chemical Society. (d) Fluorescent microscopy image of a glassy carbon bead (630 μm size), grafted with an asymmetric layer of fluoresceinamine by bipolar diazonium salt reduction. Adapted with permission from ref 23. Copyright 2013 Wiley.

The work performed by Bradley's team was a key step for the development of controlled bipolar micro- and nanoelectrodeposition; however, the process had a couple of disadvantages, such as the use of organic solvents and especially the fact that the particles had to be immobilized on a surface. As a direct consequence of this latter aspect, the process can only lead to single layer equivalents of modified objects, thus making an upscale to an industrial level difficult. New methods have been developed recently, allowing the modification of micro- and nanoparticles in an aqueous bulk phase.[30,31]

As shown in Figure 2, these technologies were used for the bulk modification of various types of carbon substrates. Anisotropic objects such as multiwall carbon nanotubes (Figure 2a), carbon fibers (Figure 2b,c), and carbon microtubes (Figure 2d,e) have been modified with metals such as gold,[30,31] platinum,[31,32] copper,[33] and nickel,[34] giving rise to a new family of hybrid carbon/metal JPs. Tuning the orientation of the electric field, its amplitude, and the viscosity of

the medium allows a fine control of the topology of the obtained deposits.[35]

The relative position of the metal with respect to the tube axis can be controlled, leading to deposits which are centered, such as the one shown in Figure 2b, and noncentered such as the one shown in Figure 2c. By using electric field pulses, the final morphology of copper-modified carbon microtubes could be controlled in terms of deposit size. The same philosophy allows also switching from a single deposit to a dumbbell-like structure, which is presented in Figure 2d.[33]

As illustrated in Figure 3, isotropic GC microparticles with different characteristic sizes could also be modified in the bulk. In comparison to anisotropic objects, which orientate themselves in the high electric field and keep a defined orientation throughout the deposition process, isotropic objects can still freely rotate, even under polarization. Therefore, in this case, a gel has been used for trapping them mechanically, in order to prevent rotation during the
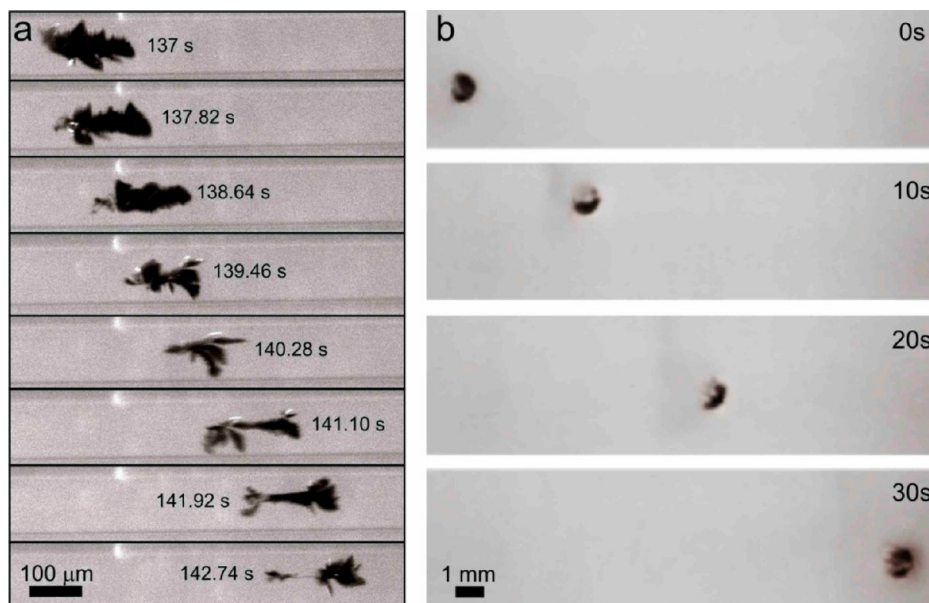
FIGURE 5. Series of optical micrographs showing translational motion of bipolar electrodes. (a) Zinc microdendrite propelled by dynamic bipolar self-regeneration. Adapted with permission from ref 51. Copyright 2010 American Chemical Society. (b) Metal bead propelled by the production of H_2 bubbles. Reprinted with permission from ref 52. Copyright (2011) Macmillan Publishers Limited.

electrodeposition.[31] Depending on the experimental conditions, the resulting carbon/gold and carbon/silver Janus spheres present a hemispherical metal coating as shown in Figure 3a and b or a single point electrodeposit like in Figure 3c.[31] Under specific conditions, where migration is the dominant mass transfer mechanism, electrodeposition of negatively charged metal species allows the formation of metal rings on spherical BPEs.[36] This phenomenon was used for generating gold and platinum rings on macro- and microspheres (see Figure 3d).[36]

Because the classical methods for generating Janus particles are often multisteps processes based on the use of interfaces,[19] those results suggest bipolar electrodeposition, which is a bulk process, as a very appropriate alternative method to obtain JPs in a single step and in large quantities. The process is very versatile in terms of composition and shape, since any type of conductive particles can be modified; the only drawback lies in the size limitation since, as stated by eq 3, very small particles, in the nanometer range, would require very high electric fields, which seems difficult to generate in a normal lab environment.

Conducting Polymers. CPs have usually a high conductivity, and their oxidation or reduction (coupled with the integration of counterions present in the medium) affects the material's band gap, changing significantly its color. Inagi et al. reported the gradient doping of CP films. In the first publication, centimeter-long films of poly(3-methylthiophene) were used as BPEs, resulting in their asymmetric doping, that could be followed visually and spectroscopically.[37] The reversibility of the process on the same polymer was demonstrated and the process was extended to two other polymers, poly(3,4-ethylenedioxythiophene) and poly(aniline).[38] The local application of the electric field on CP films was also used for their patterning.[39]

Because classic CPs, such as polypyrrole (PPy), can be electrodeposited via anodic oxidation of the soluble monomer, their electropolymerization is also possible at the anodic pole of BPEs.[29] This can be exploited for the generation of JPs comprising one CP part, as it is shown in Figure 4a, which presents a spherical Au/PPy JP. During the bipolar electroreduction of metals, which was discussed in the previous section, the oxidation that occurs at the anodic side of the substrate produces gas or other oxidation products, but the involved reactions did not lead to a modification. This counter reaction can be used for a concomitant deposition of CP and metal at opposite sides of BPEs, as it is illustrated by Figure 2e, which presents a carbon tube modified simultaneously with Cu and PPy.[33]

Deposition of Semiconductors and Insulators. The immobilization of semiconductors (SCs) and insulators on JPs can be very useful for photocatalysis or sensing applications. Bipolar electrodeposition is not limited to the formation of conductive materials, and different approaches have been recently developed in order to deposit SCs or insulators on BPEs. Direct bipolar electroreduction of CdS precursors has been demonstrated by Ramakrishnan and Shannon for the

formation of solid state gradients.[40] Alternative indirect strategies have also been reported. For instance, the local dissolution of silver nanowires at their anodic pole, in the presence of chloride ions, leads to the precipitation of AgCl at one extremity of the nanowires, as shown by Figure 4b.[31] The deposition can also be triggered by a local pH change, induced by the water electrolysis half reactions, which enable the polymerization or the precipitation of a soluble precursor.[41] This mechanism allows the deposition of silica, silicone, titanate, titanium dioxide, and organic polymers (Figure 4c) on carbon and metal particles. Organic molecules and metal nanoparticles could be inserted in these porous materials to generate functional JPs.[41] Finally, ultrathin layers of organic molecules could be electrografted based on the reduction of diazonium precursors (Figure 4d).

Bipolar Electrochemistry for Generating Motion

The fabrication and study of objects that can move in a controlled way and perform tasks at small scales has attracted huge interest across many areas of science ranging from biology to physics. Intensive recent studies have been performed, especially by the groups of Mallouk, Sen, Wang, and Schmidt in order to mimic biomotors by developing synthetic micro- and nanomotors.[42−45] The classic strategies are based on using chemically powered motors[46,47] and magnetically driven motors.[48] So far, different exciting applications such as isolation of cancer cells[49] or pollution remediation[50] have been developed using such micromotors. We are going to show in the following section that the intrinsic asymmetry provided by bipolar electrochemistry is a very appealing approach for the generation of motion of electrically conducting particles. The presented concepts are very complementary with respect to the approaches used so far in the literature, often based on dielectrophoresis and similar effects. Therefore, they are an original enrichment of the existing toolbox of mechanisms for generating motion of objects.

Translational Motion. JPs generated by bipolar electrodeposition containing a magnetic or a catalytic extremity can be used as synthetic motors. Recently, carbon microtubes with an electrochemically generated Pt tip on one side have been moved in H_2O_2 solutions.[32] The motion was caused by the generation and release of O_2 bubbles, due to the catalytic decomposition of H_2O_2 at the Pt surface. A Pt deposit immobilized in a centered way with respect to the tube axis (as it is shown for the case of a copper deposit in Figure 2b) leads to a linear motion of the swimmer.[32]
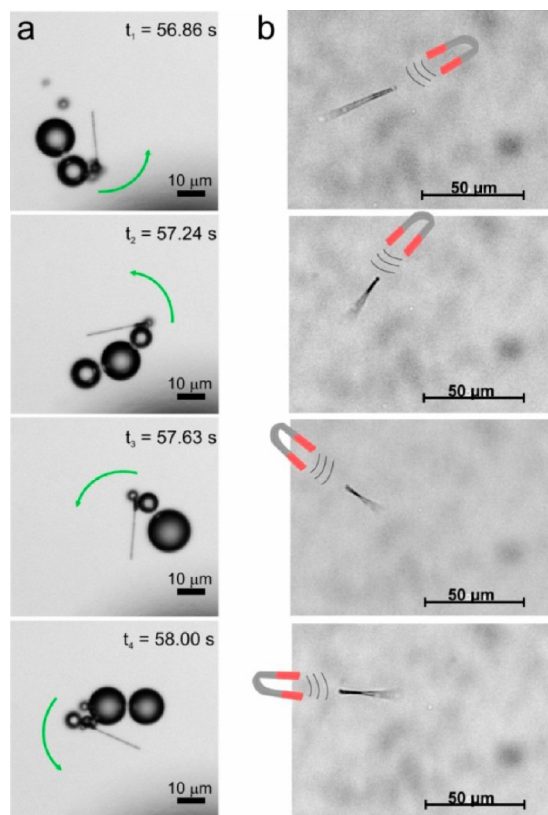
FIGURE 6. Series of optical micrographs showing rotational motion of Janus objects synthesized by bipolar electrochemistry. (a) Rotation of a carbon microtube, modified at one extremity with platinum, in a H_2O_2 solution. Reprinted from ref 32. Copyright (2011), with permission from Elsevier. (b) Rotation of a carbon microtube, modified at one extremity with nickel, under the influence of an external magnetic field. Reprinted from ref 34. Copyright (2011), with permission from Elsevier.

The asymmetric reactivity, offered by bipolar electrochemistry, can also be used directly to generate motion of isotropic particles. The first example of translational motion was based on a deposition/dissolution mechanism.[51] In this work, a Zn dendrite was placed in a capillary that was previously filled with a zinc sulfate solution. When the dendrite is acting as a BPE, its anodic pole is consumed by the oxidation, while deposition occurs at its cathodic pole, leading to its self-regeneration. This results in an apparent locomotion of the object, which can be observed in Figure 5a. This phenomenon can also be considered as a propagating chemical wave.[2]

Another strategy is based on asymmetric bubble production, due to water electrolysis at the reactive poles of a spherical BPE. Because the quantity of produced H_2 at the cathodic pole is twice as much as the amount of generated O_2 at the anodic pole, the resulting force rolls the bead in a controlled way.[52] A possibility to enhance the propulsion speed and to better control its direction is to quench one of
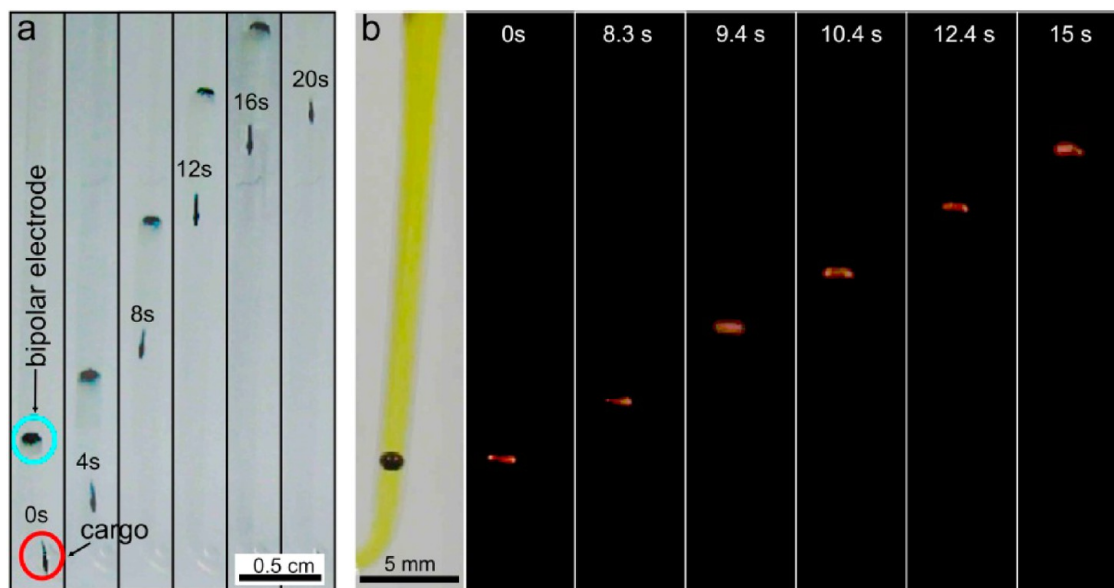
FIGURE 7. Series of optical micrographs showing levitation of bipolar electrodes. (a) Cargo lifting of a polymer capsule by a glassy carbon bipolar electrode. Adapted from ref 53 with permission of The Royal Society of Chemistry. (b) Coupling levitation with electrogenerated chemiluminescence. The left image was taken under white light and the other images were taken in the dark. Adapted with permission from ref 55. Copyright Wiley (2012).

the bubble producing reactions, by adding to the solution a sacrificial molecule (which is easier to oxidize or to reduce than water), thus allowing the bubble production to occur only at one bead pole. Translational motion has been induced on millimeter-sized metal beads, and on micrometer-sized carbon beads in polydimethylsiloxane (PDMS) microchannels (Figure 5b).[52]

Rotational Motion. The catalytic generation of O_2 bubbles in H_2O_2 media on carbon/Pt JPs, synthesized by bipolar electrodeposition, can also be used for generating rotational motion.[32] Indeed, a Pt deposit, noncentered with respect to the carbon tube axis (as the one shown in Figure 2c for the case of Cu), induces the rotation of the JP in a H_2O_2 solution. Such a motion is illustrated in Figure 6a.

Alternatively, JPs containing a ferromagnetic part can also be used as microrotors in this context. Carbon microtubes modified at one extremity with a Ni particle could be rotated using an external magnetic field, as shown in Figure 6b.[34]

The field induced bubble production on a BPE was also employed to generate rotations. Two types of bipolar rotors, fabricated using cross-shaped carbon sheets, supported by an axis at their center of mass, were designed.[52] The first type, which rotates in a horizontal plane, involves H_2 and O_2 evolution. The second one rotates in a vertical plane and involves water reduction and hydroquinone oxidation. In this case, the buoyancy generated by the H_2 bubbles was used for increasing the rotor speed.[52]

Levitation. The translation motions previously discussed were achieved in a horizontal plane. More recently, the levitation of particles in capillaries has been reported. The mechanism involves the reduction of water at the cathodic pole of the BPE.[53] In this configuration, bubbles are generated underneath a GC bead, which acts as a BPE. The bubbles are confined by the bead and the capillary wall, which generates enough buoyancy to lift the bead.[53] As shown in Figure 7a, this system was employed for dragging a small cargo attached to the BPE with a polymeric wire. When replacing a straight capillary by a conically shaped one, the periodic bubble accumulation and release induced the generation of an alternating motion instead of a continuous one (yo-yo).[53]

In all the examples of motors activated by bipolar electrogeneration of bubbles described above, the anodic counter reactions were not useful in the context of propulsion. They can therefore be replaced by other electrochemical reactions that may induce an additional functionality. Electrogenerated chemiluminescence (ECL) is the process of light emission by the excited state of a luminophore, which results from an initial electrochemical reaction at the electrode surface. A model system used for analytical purposes consists in the oxidation of the luminophore $Ru(bpy)_3^{2+}$ with tri-*n*-propylamine as a co-reactant.[54] As shown in Figure 7b, it has been recently demonstrated that ECL can be successfully coupled to the levitation of a BPE, generating light at its anodic pole.[55] In this case, ECL provides a direct monitoring

of the BPE motion, which could be very useful for localizing micromotors.

Conclusion

Bipolar electrochemistry has recently attracted an increasing attention. The theoretical foundations of the technique are very well understood and described,[56−58] which allows one to explore a variety of original experimental setups. The advantages of the technique, such as its wireless aspect and the unique characteristics of the BPEs, have been used for applications in several domains. In materials science, it has been employed for the single-step synthesis of molecular and materials gradients on conductive macroscopic objects. JPs have been generated in the bulk phase by depositing different materials such as metals, conducting polymers, semiconductors, insulators, and molecular layers at one or both reactive poles of anisotropic or isotropic BPEs of different nature.

The intrinsic break of symmetry provided by the technique can also be used for designing or powering moving objects. On the one hand, the catalytic or magnetic properties of JPs synthesized by bipolar electrodeposition have been used for propelling them. On the other hand, bipolar electrochemistry also provides a straightforward approach for directly inducing motion of isotropic conductive particles. Mechanisms based on dynamic self-regeneration of a BPE, or a localized bubble production were developed for the translation of objects. Bubble-powered motors can also rotate or levitate and have been coupled with the emission of light.

These concepts hold great promises for future developments based on the use of bipolar electrochemistry in the two major fields of materials science and the generation of controlled motion. As a consequence, exciting new scientific opportunities should arise, especially when combing both aspects, in order to introduce additional functionalities in these systems, such as an emission of light[59] or a catalytic activity.[60] In those cases, the presence of an external electric field could for example induce motion of an object, which can be tracked by the emission of light and carry out simultaneously certain tasks, such as cargo lifting or the catalytic conversion of either pollutants, analytes, or fuel precursors, resulting in an unprecedented multifunctionality of the objects. We therefore expect that bipolar electrochemistry will undergo a rapid further development in the near future and lead to promising new applications that should go far beyond the materials science and motion aspects described in this review.

BIOGRAPHICAL INFORMATION

Gabriel Loget received his Bachelor degree in Chemistry and his Master degree in Molecular Chemistry from the University of Rennes (France). He recently completed his Ph.D. at the University of Bordeaux (France) under the supervision of Pr. Alexander Kuhn. His Ph.D. focused on developing new concepts for the synthesis of Janus-type objects and the locomotion of particles. He is currently a postdoctoral researcher in the group of Pr. Robert M. Corn at the University of California Irvine.

Dodzi Zigah has a Master degree in electrochemistry from the University Denis Diderot (Paris, France). In 2009, he obtained a Ph.D in electrochemistry from the University of Rennes (France). After a postdoc position at the University of Texas in Austin, he joined the faculty of the University of Bordeaux in 2010 as an assistant professor. His current research focuses on localized surface modification and characterization using electrochemistry in order to design original sensors.

Laurent Bouffier received a Master degree in molecular chemistry and a Ph.D. in organic chemistry from the University Joseph Fourier (UJF) of Grenoble (France). After a postdoctoral position at UJF, he joined the University of Liverpool (U.K.) for two PDRA positions. In 2010, he has moved to the University of Bordeaux (France) as a CNRS scientist. His background includes organic synthesis, electrochemical biosensors, molecular electronics, and micro/nanomaterials. His current research is dedicated to the preparation of hybrid materials by bipolar electrochemistry and the development of new electroanalytical biosensors.

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Alexander Kuhn obtained a Master degree in Chemistry from the Technical University of Munich (Germany) and a Ph.D. in Physical Chemistry from the University of Bordeaux (France). After a postdoc position at the California Institute of Technology, he moved to the University of Bordeaux as an assistant professor and is since 2000 a full professor. His main research interests are in electrochemistry, surface modification and nanoscience. In recent years, he has made contributions to the fields of bioelectrochemistry, electroanalysis, and the rational design of electrode surfaces, as well as the synthesis of complex micro- or nanoobjects.

FOOTNOTES

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