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Indirect Bipolar Electrodeposition

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Supporting Information

ABSTRACT: Based on the principles of bipolar electrochemistry, localized pH gradients are generated at the surface of conducting particles in solution. This allows the toposelective deposition of inorganic and organic polymer layers via a pH-triggered precipitation mechanism. Due to the intrinsic symmetry breaking of the process, the concept can be used to generate in a straightforward way Janus particles, with one section consisting of deposits obtained from non-electroactive precursors. These indirect electrodeposits, such as SiO_2, TiO_2, or electrophoretic paints, can be further used as an immobilization matrix for other species like dyes or nanoparticles, thus opening promising perspectives for the synthesis of a variety of bifunctional objects with a controlled shape.

The controlled surface modification of micro- and nanoparticles is of importance for an almost unlimited variety of applications. In this context a special effort is devoted to the synthesis of anisotropic objects, also referred to as Janus particles, that has attracted an increasing interest in the past 10 years.[1−3] These objects are key components of a significant number of applications. As an example, Janus particles with conductivity anisotropy such as conducting−insulating combinations can be used as motile objects[4] or in detectors.[5] Conducting−semiconducting Janus objects have photocatalytic properties.[6,7] Moreover, industrial applications for Janus objects have already been considered, one example being the development of gyricon balls[8] that might serve as pixels in electronic paper.[9]

Many different methods exist for the generation of Janus particles,[10] and one of the very few approaches allowing their production in the true bulk phase is bipolar electrochemistry.[11] However, so far this concept has been limited to deposits obtained from electroactive precursors, such as metal salts for deposition of metal[11−14] or monomers for the synthesis of conducting polymers.[14,15] This is a severe limitation, as many interesting materials cannot be obtained directly by electrodeposition or electropolymerization. Here we present an original and complementary approach that allows us to extend the concept of bipolar electrodeposition to the indirect electrogeneration of materials that cannot be obtained from electroactive precursors.

Bipolar electrochemistry relies on the fact that, when a conducting object is positioned in a solution under the influence of an electric field, a polarization of the two sides of the object occurs. The associated polarization voltage with respect to the solution is proportional to the electric field E and the object length d:

$$\Delta V = Ed \tag{1}$$

If ΔV is high enough, electrochemical reactions can be carried out simultaneously at both extremities of the object, reductions at the cathodic pole and oxidations at the anodic pole.[16,17] Bipolar electrochemistry has been recently used for analysis,[18−20] electronics,[21,22] propulsion,[23,24] and materials science.[11−15,25−27] So far, all reported surface modifications carried out by bipolar electrochemistry have been achieved with direct electroreduction or electrooxidation at the object/solvent interface, leading to toposelective deposits. The concept described herein is based on the fact that, by bipolar electrochemistry, it is also possible, like in classic electrochemistry, to generate pH changes at the electrode/solution interface. Such a pH change in the vicinity of the polarized object can be used to indirectly deposit organic layers such as electrophoretic deposition paints (EDPs)[28] or inorganic layers using sol−gel chemistry.[29,30] In addition to their attractive insulating properties, these materials can also be used as encapsulation matrices to trap a wide variety of species such as dyes[31] or biomolecules.[32]

As a proof-of-principle, we illustrate in the following this concept of indirect bipolar electrodeposition (IBED) for the localized and asymmetric generation of EDP, silica, silicone, titanate, and titanium dioxide.

The entire process is based on the classic water electrolysis half-reactions (see Figure 1a):

$$H_2O \rightarrow 2H^+ + {}^{1}\!/_{2}O_2 + 2e^- \qquad E_1^0 = 1.23\ \text{V vs NHE} \tag{2}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E_2^0 = 0\ \text{V vs NHE} \tag{3}$$

They occur at both sides of the conducing object if, in a first approximation, the applied electric field induces a polarization potential ΔV_{min} between the two extremities of the object that is larger than the difference between the formal potentials of the involved redox couples: $E_1^0 - E_2^0 = 1.23$ V. However, variable overpotentials due to potential drops at the electrodes and in the solution will also need to be added to this value. In order to directly visualize this phenomenon, we carried out a preliminary experiment in a cell containing a pH indicator.[33]

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The cell was composed of two feeder electrodes and one carbon disc at the center which acted as a bipolar electrode. In this experiment the carbon disc diameter d is 6 mm and the electric field value E is 8.8 V cm^{-1}. Using eq 1, ΔV is found to be equal to 5.3 V, a value that, being superior to the thermodynamic threshold value of 1.23 V, allows half-reactions 2 and 3 to occur. At the feeder anode and cathode, these reactions induce the expected pH variations. In addition, strong pH changes are also observed at the two sides of the bipolar electrode. Again these pH changes are due to water oxidation at the anodic pole and simultaneous water reduction at the cathodic pole, generating acid (red color) and alkaline (blue color) gradients, respectively (Figure 1b). Based on this experiment, which shows clearly that pH in the vicinity of conducting objects can be controlled by bipolar electrochemistry, the IBED process depicted in Figure 1a becomes straightforward.

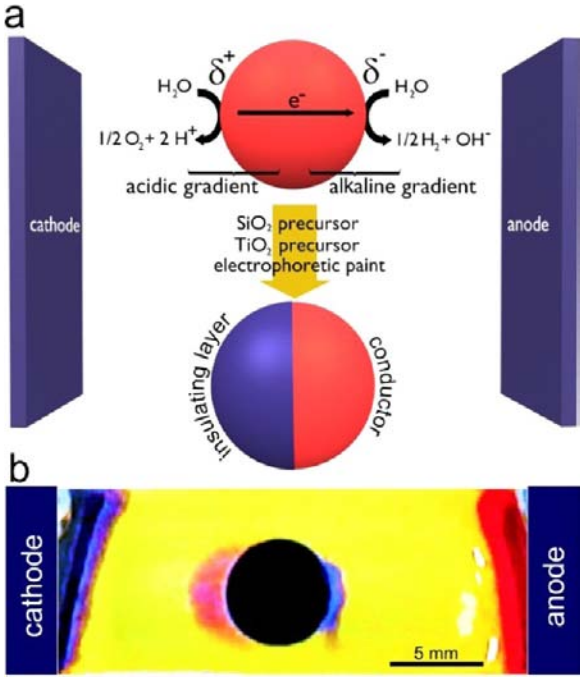

Figure 1. (a) Scheme of the indirect bipolar electrodeposition (IBED) principle. (b) Visualization of the pH evolution at a bipolar electrode, revealed by using a universal pH indicator. Blue corresponds to basic pH, and red corresponds to acid pH.

The sol–gel approach is a class of processes in which a solid phase is formed through gelation of a colloidal suspension (sol).[34] Probably the most used sol–gel processes are silicon based. In this case, a sol is first formed by the hydrolysis of an alkoxysilane precursor (n = 1–3, R and R′ are different functional groups):

$$R_nSi(OR')_{4-n} + (4-n)H_2O \rightarrow R_nSi(OH)_{4-n} + (4-n)R'OH \quad (4)$$

Polycondensation of the hydrolyzed precursor, catalyzed by hydroxyl ions, can then be achieved by increasing the pH:

$$2R_nSi(OH)_{4-n} \rightarrow R_n(OH)_{3-n}Si{-}O{-}Si(OH)_{3-n}R_n + H_2O \quad (5)$$

This polymerization leads to the final polysiloxane. Playing with the functional groups R allows us to control the degree of cross-linking and thus the material properties. Working with various precursors gives access to a large range of polysiloxane materials, starting from silica when using tetraethylorthosilicate (TEOS), but also much more sophisticated materials with a wide variety of chemical and physical features. Due to the hydroxide generation, polycondensation occurs at the cathodic pole of the bipolar electrode.

The scanning electron micrograph (SEM) in Figure 2a shows a sub-millimeter carbon bead which has been modified using an electric field of 107 V cm^{-1} and a sol containing TEOS precursor (see SI for details). The silica modification is clearly observable as the brightest part of the Janus object. The cracks present in the deposit illustrate the poor adhesion and brittle character of the material, a property that can be tuned by controlling the degree of cross-linking of the polysiloxane. Figure 2b shows a similar bead modified under the same conditions but using methyltrimethoxysilane (MTMOS) as a precursor. The methyl group on the silicon leads to a polycondensation of only three positions around the Si atom, which generates a less cross-linked polysiloxane deposit that covers the substrate (Figure 2b) more smoothly than silica, due to a higher flexibility.

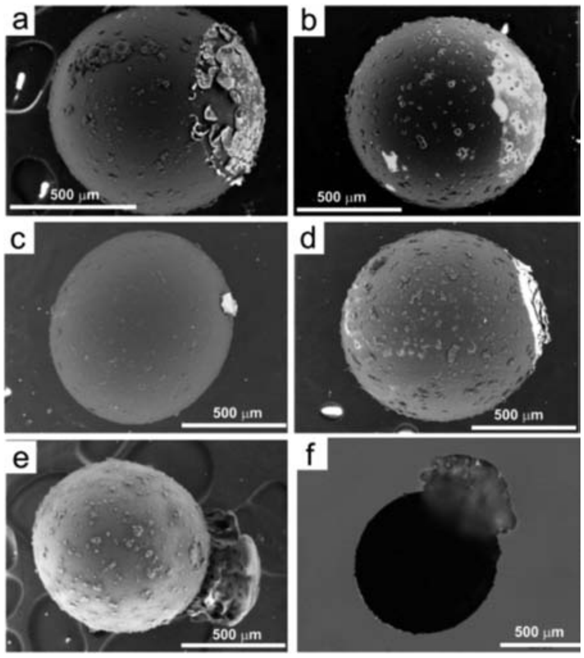

Figure 2. Modification of sub-millimeter-sized glassy carbon beads with different materials by IBED. SEM picture of a glassy carbon bead modified with (a) silica using a TEOS-based sol–gel, (b) silicone using a MTMOS-based sol–gel, (c) titanate using an electric field of 71 V cm^{-1}, (d) titanate using an electric field of 214 V cm^{-1}, and (e) EDP. (f) Optical micrograph showing a glassy carbon bead modified with EDP.

Other types of materials can also be deposited using sol–gel procedures. Because of the importance of TiO_2 for many topics such as photovoltaics or water splitting, we show here that bipolar electrodeposition can generate Janus objects with TiO_2. Ohya et al. reported the preparation of a stable transparent titanate colloidal solution by mixing Ti(IV) tetraisopropoxide and tetramethylammonium hydroxide (TMAOH).[35] This solution, containing colloids of layered poly-Ti(IV)oxo acid species, stabilized by bulky TMA^+ counterions, can be used as a sol for the anodic deposition of titanate films.[36] The indirect bipolar electrodeposition was carried out using two electric field values. First experiments were performed at $E = 71$ V cm^{-1}. The typical asymmetric particle in Figure 2c shows a small titanate deposit at one extremity. As it is clearly demonstrated in Figure 2d, a higher electric field value, in this case $E = 214$ V cm^{-1}, leads to bigger deposits, which cover a larger area of the glassy carbon particle. This demonstrates that, when playing with the two crucial parameters of eq 1, namely the characteristic dimensions of the objects and the applied external voltage, one can control the portion of the modified area of the particles. X-ray diffraction (XRD) experiments reveal that calcination of the titanate deposit at 450 °C during 4 h leads to crystalline anatase (see Figure S3 for XRD spectrum).

EDPs are widely used in the automobile industry as anti-corrosion layers[28] and have recently gained additional interest because they can also be used as efficient matrices for biomolecule encapsulation.[32,37] The anodic EDP we used in this work (Resydrol AY498w/35WA) is a mixture of micellar polyacrylates. Due to the presence of carboxyl groups, the water-soluble form of the polymer is negatively charged. A pH drop induced by reaction 2 leads to neutralization of the carboxyl groups and precipitation of the polymer at the surface. Figure 2e shows a SEM picture of the snowman-like Janus structure obtained by modifying a carbon bead with EDP, using an electric field of 71 V·cm^{-1}. The reflectivity contrast between the two materials is revealed by the optical micrograph presented in Figure 2f.

The cell design that has already been developed for the bipolar electrodeposition of metals[11] allows generating the present Janus particles in the bulk phase. Figure 3a shows a typical image, obtained for carbon particles modified with EDP in the bulk. In order to demonstrate the versatility of the approach, we have used this time a cathodic EDP (BASF Coatings FT23-0510).

As can be seen from the zoom-in on one of the particles in Figure 3b, the deposit is quite porous, which facilitates further functionalization in an asymmetric way. As an example for this post-functionalization, the Janus beads were exposed to a solution of fluorescein overnight. The dye exclusively adsorbed on the side with the porous EDP layer, as illustrated by Figure 3c. This opens interesting perspectives for the immobilization of other compounds, such as redox-active molecules, pigments, enzymes, catalysts, drugs, etc. In preliminary experiments in this direction, it was possible to trap Al_2O_3, TiO_2, and Au nanoparticles in the different matrices (see SI).

Such deposits can be generated not only on carbon particles but also on many different kinds of conducting substrates. In order to validate the general nature of the approach, we tested two types of metal particles.

First, we used amorphous Pt particles with sizes of a few tenths of micrometers and with a non-spherical shape (Figure 4a). The modification leads to Janus-type objects with an EDP part, as shown in Figure 4b, where the darkest part is the EDP deposit, capping the Pt particle. One can imagine these particles finding interesting applications for heterogeneous catalysis in two-phase systems.[38] Finally, spherical Ni particles with a diameter of a few micrometers (Figure 4c) were also modified with EDP, in order to generate ferromagnetic Janus particles, as demonstrated in Figure 4d.

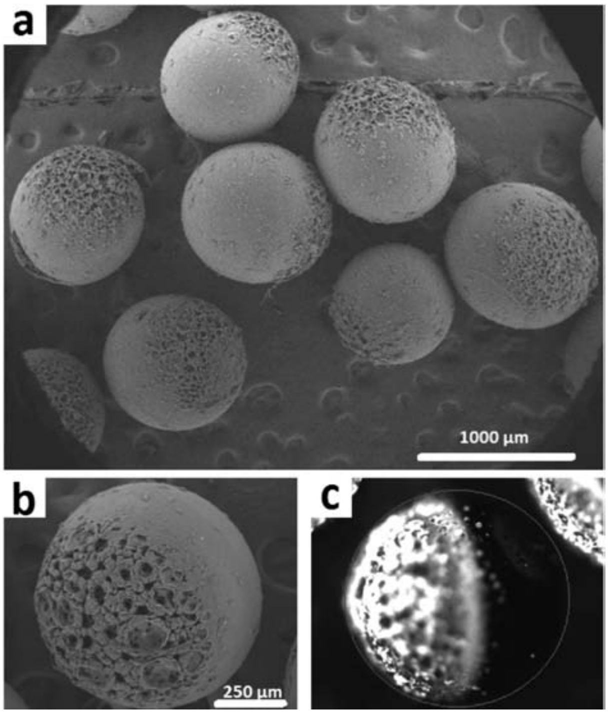

Figure 3. (a) SEM image of the carbon particles (600−1000 μm) modified with cathodic EDP by applying an electric field of 45 kV·m^{-1} for 2 s. (b) Zoom-in on one of the particles illustrating the intrinsic porosity of the deposit. (c) Fluorescent microscope image of an EDP-modified particle for which the pores have been filled with fluorescent dye. The circle indicates the global shape of the particle.

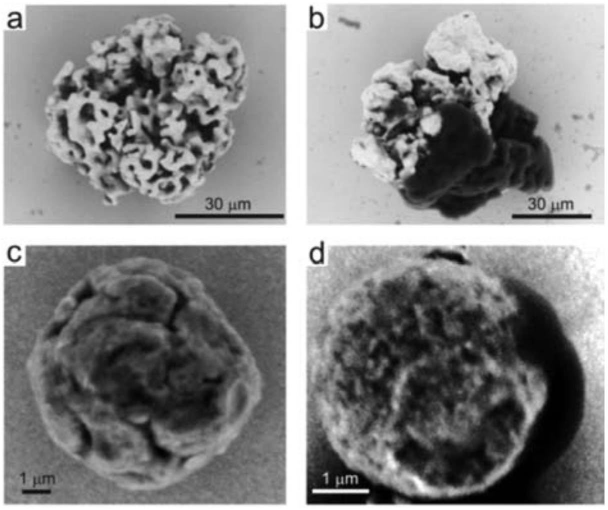

Figure 4. Metal microparticles modified with anodic EDP by IBED. SEM image of (a) an amorphous Pt particle, (b) an amorphous Pt particle modified with EDP by IBED, (c) a spherical Ni particle, and (d) a spherical Ni particle modified with EDP by IDEP.

All these results demonstrate for the first time that insulating materials, such as metal oxides or EDPs, can be deposited by IBED from non-electroactive precursors on various substrates, leading to Janus objects with a conductivity anisotropy controlled at the microscale.

The approach does not involve a direct electron transfer between the substrate and the deposit precursor, but rather takes advantage of a local pH change around the conducting particle, which leads to controlled polymerization and/or precipitation of the insulating deposit. The versatility of the process has been demonstrated in terms of material combinations since silica, silicone, titanate, crystalline titanium dioxide, and organic insulating polymers have been successfully deposited on different materials. The concept has been validated for particles with different characteristic sizes to generate Janus objects. The encapsulating capabilities of the deposits were explored by the formation of fluorescent Janus objects. These results open new perspectives for the straightforward generation of Janus particles that could be used in important applications such as e-paper,[39] sensing,[5] micropropellers, photovoltaics, water splitting, or heterogeneous catalysis.[6,7,38]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Description of several examples for encapsulating dyes, and experimental details concerning the synthesis and characterization of the Janus particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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