Breaking the symmetry of micro- and nanoobjects by bipolar electrochemistry

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ABSTRACT

Janus particles are defined as micro- or nano- particles owning two sides of different chemistry [1]. It has been demonstrated that they can be used as key-components in applications such as catalysis [2], medical therapy [3], detection [4] or display technologies [5]. However, the synthesis of Janus particles is still challenging, and achieving a cost effective large-scale production remains an issue that slows down their industrial application. So far, a great majority of methods used to produce these particles breaks the symmetry by using a surface or interface [6]. This makes the preparation of large quantities rather difficult since those processes involve a 2D reaction space, and thus, lead only to monolayer equivalents of material. We demonstrated that it is possible to use the concept of bipolar electrochemistry to generate anisotropy on conductive particles in the bulk phase [7]. This technology allows tailoring the shape and the position of the deposited materials that can be either a metal, a polymer, an organic layer or even a semi conductor [8], [9], [10], [11], [12].

Keywords: Janus particles, bipolar electrochemistry, bulk synthesis.

1 INTRODUCTION

Dissymmetric functionalization of micro- and nanoobjects is of major importance to study, for example, directed self-assembly, but also for many applications ranging from electronic paper to sensing and catalysis. Various approaches to generate dissymmetric particles have been reported in the recent literature. These Janus-type particles have been obtained either by protection/deprotection mechanisms [13], focused laser-induced reactions [14], co-jetting of parallel polymer solutions under the influence of an electrical field [15], anisotropic electroless deposition [16], or with microfluidic techniques [17]. However, so far most of the methods used to generate such objects need to break the symmetry by introducing interfaces like in the case of sputtering [18], [19], stamp coating [20], [21], and Langmuir-Blodgett-based techniques [22]. This makes the preparation of large quantities rather difficult.

Thus, there is an increasing interest in developing alternative methods to replace the two-dimensional approaches by truly three-dimensional techniques allowing a scaled-up production of Janus objects to larger quantities by using bulk procedures [23].

In this context an attractive method uses the concept of bipolar electrochemistry. In brief, when a conducting object in solution is placed in a strong electric field between two electrodes a polarization with respect to the solution's potential occurs that is proportional to the electric field *E* and the characteristic dimension *r* of the object.

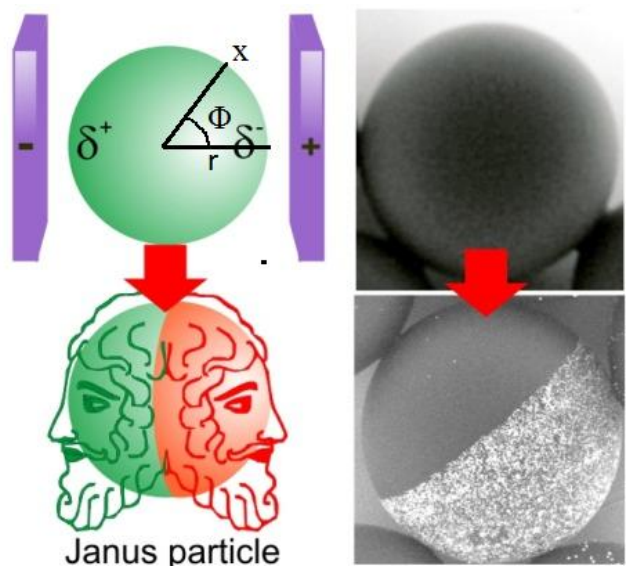

Figure 1. Polarization of a conducting particle in an electric field for Janus particle synthesis. Adapted from [10]

Theoretically, the potential difference arising between the two ends of a conductive particle with respect to the solution's potential is given by Equation 1

$$\eta_x = E\ r \cos\Phi \qquad (1)$$

With η_x being the polarization at a given point x at the surface of the particle, one can easily calculate that the maximum potential difference between the two opposite sides of the object is given by Equation 2:

$$\Delta V_{max} = 2\ E\ r \qquad (2)$$

In order to carry out two different redox reactions at the opposite sides of the conductive object (oxidation at the left side and reduction at the right side) ΔV_{max} has to be at least equal to the difference of the formal potentials of the two redox reactions. Two typical redox reactions that could take place in an aqueous environment to generate a gold deposit might be the following ones:

$$[AuCl_4]^-_{(aq)} + 3e^- \rightarrow Au^0_{(s)} + 4Cl^-_{(aq)} \qquad E° = +0.99\ V$$

$$2H_2O_{(l)} \leftrightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^- \qquad E° = +1.23\ V$$

It immediately follows that the polarization has to generate a potential difference of at least 0.24 V. This concept has been widely used in industrial electrochemical reactors. However adapting it to micrometer sized objects is quite problematic as the electric field must achieve values of up to $MV.m^{-1}$, leading to high bubble production at the electrodes that disturbs the orientation of the object in the electric field, and induces also solvent evaporation and convection due to the ohmic heating. Nevertheless, using the appropriate reactor design and experimental conditions, a large number of different Janus particles were produced. The driving force being a difference of potential, any type of electrochemical reaction can theoretically be achieved on a conducting substrate, allowing a very rich variety of combinations of materials like metal, metal oxide, semiconductors, polymers or organic layers. Taking advantage of water oxidation and reduction, it is also possible to trigger localized precipitation of electroinactive species thanks to the locally induced pH gradients.

2 DIRECT BIPOLAR ELECTRODEPOSITION (DBED)

Carbon objects, such as micrometer sized tubes (Fig. 2a) and beads with sizes covering two orders of magnitude (Fig. 2d, 2f and 2i) have been modified with gold, platinum or silver. At the end of the bipolar electrodeposition experiment, the modification is clearly visible under the scanning electron microscopy (SEM) due to the high electronic contrast of the different materials (Fig. 2). From a process point of view, after parameter screening and optimization, yields of up to 70% were achieved for a model reaction, namely gold deposition on 200 to 400 µm glassy carbon beads, as one can see on Fig. 2e. This value has been determined as the ratio between the number of Janus beads and the total number of beads by simply counting them on SEM pictures. Further optimization of this yield, as well as its extension to other types of Janus particle is in progress in the laboratory.

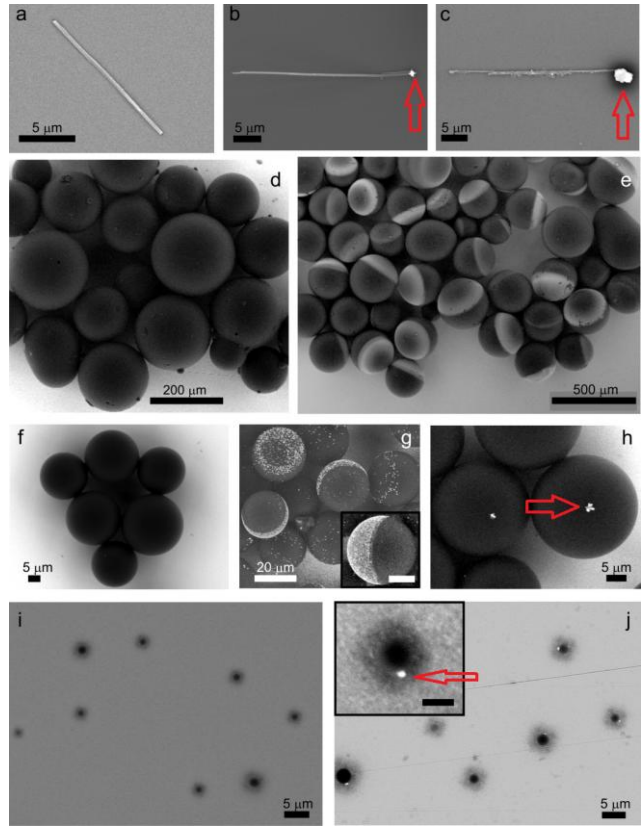

Figure 2. Anisotropic and isotropic carbon-metal Janus particles. SEM pictures of the particles before and after bipolar electrodeposition. (a) Unmodified carbon tube. (b) Carbon tube modified with gold. (c) Carbon tube modified with platinum. (d) Unmodified glassy carbon beads with diameters ranging from 200 to 400 µm. (e) Glassy carbon beads with diameters ranging from 200 to 400 µm modified with gold. (f) Unmodified glassy carbon beads with diameters ranging from 20 to 50 µm. (g) Glassy carbon beads with diameters ranging from 20 to 50 µm modified with gold. Inset: detail of a Janus bead (scale bar 10 µm). (h) Glassy carbon beads modified with silver. (i) Unmodified micrometer sized glassy carbon beads. (j) Micrometer glassy-carbon bead modified with gold. Inset: detail of a bead modified with gold (scale bar 1 µm). Adapted from [10]

3 INDIRECT BIPOLAR ELECTRODEPOSITION (IBED)

Direct bipolar electrodeposition is limited to deposits obtained from electroactive precursors, such as metal salts for deposition of metal or monomers for the synthesis of conducting polymers. This is a severe limitation as many interesting materials cannot be obtained directly by electrodeposition or electropolymerisation. Here we present an original and complementary approach that allows

extending the concept of bipolar electrodeposition to the indirect electrogeneration of materials that cannot be obtained from electroactive precursors.

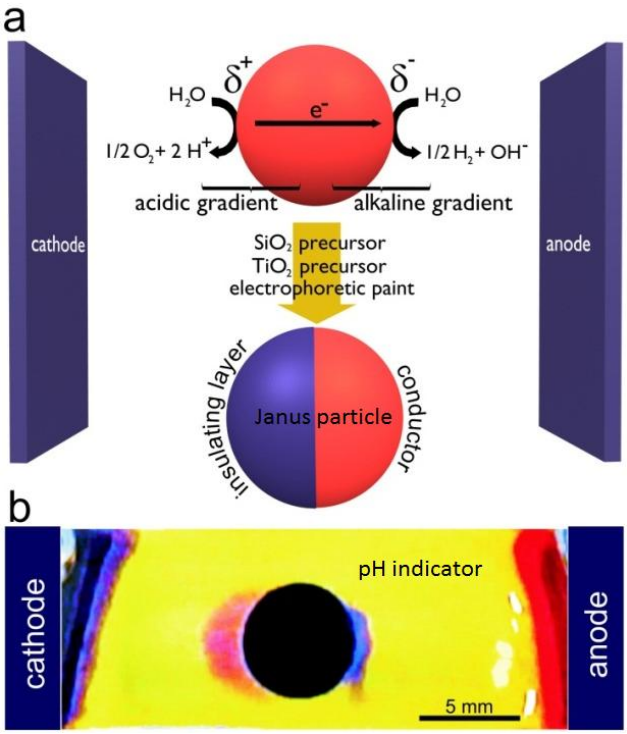

Figure 3: a) Scheme of the indirect bipolar electrodeposition (IBED) principle. b) Visualization of the pH evolution at a bipolar electrode, revealed by using a universal pH indicator. Blue corresponds to basic pH and pink corresponds to acid pH. Adapted from [12].

The concept, described in figure 3, is based on the fact that it is also possible, like in classic electrochemistry, to generate pH changes at the electrode/solution interface by bipolar electrochemistry. Such a pH change in the vicinity of the polarized object can be used to deposit indirectly organic layers such as electrophoretic deposition paints (EDPs), or inorganic layers using sol-gel chemistry such as TiO_2 or silica. In addition to their attractive insulating properties, these materials can also be used as encapsulation matrix and consequently trap a wide variety of species such as dyes or biomolecules.
The process to generate pH gradients is based on the classic water electrolysis half-reactions:

$$\mathbf{2H_2O_{(l)} + 2e^- \leftrightarrow 2OH^-_{(aq)} + H_{2(g)}} \qquad \mathbf{E° = 0\ V}$$

$$\mathbf{2H_2O_{(l)} \leftrightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-} \qquad \mathbf{E° = +1.23\ V}$$

3.1 Inorganic deposits

Janus particles depicted on figure 4 have been achieved using either an acidic pH change for TiO_2 deposition or an alkaline one for silica precipitation.

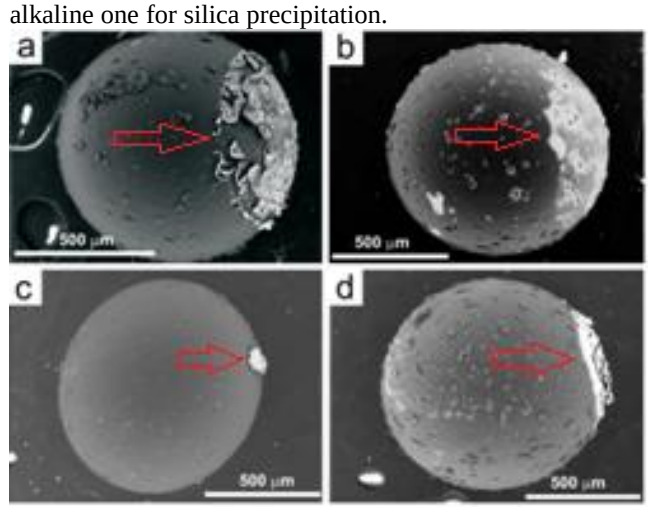

Figure 4. Modification of submillimeter-sized carbon beads with different materials by indirect bipolar electrodeposition (IBED). a) SEM picture of a glassy carbon bead modified with silica using a TEOS based sol-gel. b) SEM picture of a glassy carbon bead modified with a silicone using a MTMOS based sol-gel. c) SEM picture of a glassy carbon bead modified with titanate using a weak electric field. d) SEM picture of a glassy carbon bead modified with titanate using a strong electric field. Adapted from [12].

3.2 Organic deposits

Electrophoretic paints (EDPs) have been widely used for a long time as anti-corrosion layers in car and can industries, and have recently gained additional interest because they can also be used as efficient matrices for biomolecule encapsulation. The cathodic EDP used in this work (BASF coatings FT23-0510) implies that it will precipitate on the alkaline side of the polarized object, due to the presence of protonated amino groups on the polymer backbone that become neutral as pH increases.
Figure 5a shows a typical image obtained for carbon particles modified with EDP in the bulk. As can be seen from the zoom on one of the particles (Fig. 5b) the deposit is quite porous which allows further functionalization in an asymmetric way. As an example for this post-functionalisation the Janus beads have been exposed to a solution of fluorescein overnight. The dye exclusively adsorbs on the side with the porous EDP layer as illustrated by Figure 5c. This opens interesting perspectives for the immobilisation of other compounds such as redox active molecules, pigments, enzymes, catalysts, etc. In preliminary experiments in this direction it was also possible to trap Al_2O_3, TiO_2 and Au nanoparticles in the different matrices.

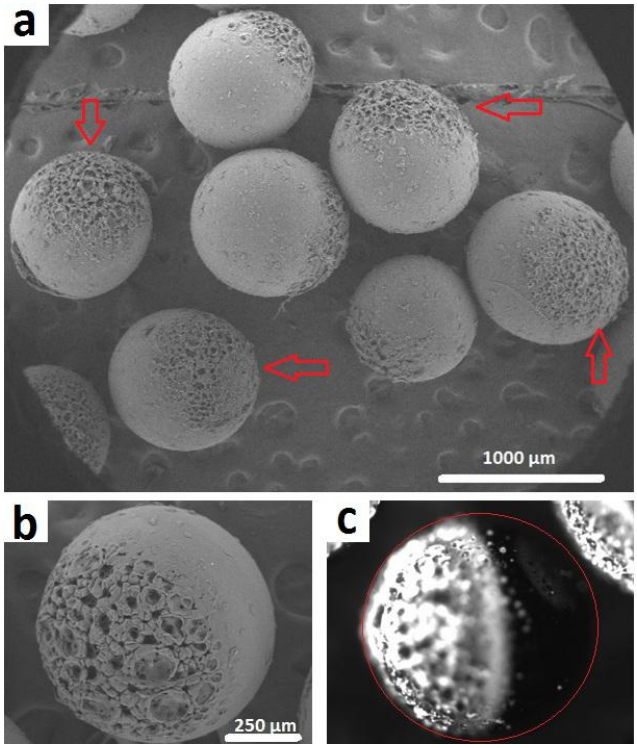

Figure 5. a) SEM image of the carbon particles (600-1000 µm) modified with cathodic EDP by applying an electric field of 45 kV.m^{-1} for 2 s. b) Zoom on one of the particles illustrating the intrinsic porosity of the deposit. c) Fluorescent microscope image of a EDP modified particle with pores filled with fluorescent dye. Adapted from [12].

4 CONCLUSION

In conclusion, we propose a new technology for the production of Janus particles, which has two main advantages. The first point is its versatility. The generation of a wide range of different Janus particles with respect to particle material, size and shape is now possible using one and the same technology. Furthermore there is also a large choice for the type of deposited materials (metals, polymers, metal salts, etc). Many different solvents, conducting particles and redox reagents are usable, which results in a very rich variety of possible combinations. Moreover, electroinactive species can also be used as long a precipitation can be triggered by a pH stimulus. The second and surely most important point resides in the fact that this is a true bulk process that does not need any surface or interface to break the symmetry. There are no indications that this process cannot be adapted to production volumes exceeding by far the ones reported here. This allows an industrial production of Janus particles with a rational design and a high added value. Finally the process is quite straight forward and easy to implement, as the basic ingredients are only an electric power source and a reservoir with two separator elements. This simple and cheap equipment should allow a low-cost production of Janus-type nano- and microobjects with a sophisticated and highly controlled composition.

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REFERENCES

[1] P. G. de Genns, Rev. Mod. Phys., 64, 645, 1992.
[2] D. J. Cole-Hamilton, Science, 327, 41, 2010.
[3] S.-H. Hu, X. Gao, J. Am. Chem. Soc., 132, 7234, 2010.
[4] M. Himmelhaus, H. Takei, Sens. Actuat. B Chem., 63, 24, 2000.
[5] B. Comiskey, J. D. Albert, H. Yoshizawa, J. Jacobson, Nature, 394, 253, 1998.
[6] G. Loget, A. Kuhn, J. Mater. Chem., 22, 15457, 2012.
[7] C. Warakulwit et al, Nanoletters, 8, 500, 2008.
[8] G. Loget, et al, Electrochemical Acta, 55, 8116, 2010
[9] G. Loget, et al, Chemistry of Materials, 23, 2595, 2011.
[10] G. Loget, J. Roche, A. Kuhn, Adv. Mat., 24, 5111, 2012.
[11] Z. Fattah, J. Roche, P. Garrigue, D. Zigah, L. Bouffier, A. Kuhn, ChemPhysChem, DOI: 10.1002/cphc.201300068, 2013.
[12] G. Loget, J. Roche, E. Gianessi, L. Bouffier, A. Kuhn, J. Am. Chem. Soc., 134 (49), 20033–20036, 2012
[13] Perro, A.; Reculusa, S.; Pereira, F.; Delville, M.-H.; Mingotaud, C.; Duguet, E.; Bourgeat-Lami, E.; Ravaine, S. J. Chem. Soc., Chem. Comm., 44, 5542, 2005.
[14] Hugonnot, E.; Delville, M.-H.; Delville, J.-P. Appl. Surf. Sci, 248, 470, 2005.
[15] Roh, K.-H., et al, J. Nature Mat., 4, 759, 2005.
[16] Cui, J.-Q.; Kretzschmar, I. Langmuir, 22, 8281, 2006.
[17] Nisisako, T., et al. Adv.Mater., 18, 1152, 2006.
[18] Takei, H.; Shimizu, N. Langmuir, 13, 1865, 1997.
[19] Lu, Y.; Xiong, H.; Jiang, X.; Xia, Y.; Prentiss, M.; Whitesides, G. M. J.Am.Chem.Soc., 125, 12724, 2003.
[20] Cayre, O.; Paunov, V. N.; Velev, O. D. J.Mater.Chem., 13, 2445, 2003.
[21] Paunov, V. N.; Cayre, O. J. Adv.Mater., 16, 788, 2004.
[22] Fujimoto, et al, H. Langmuir, 15, 4630, 1999.
[23] Hong, L.; Cacciuto, A.; Luijten, E.; Granick, S. Nano Lett., 6, 2510, 2006.