

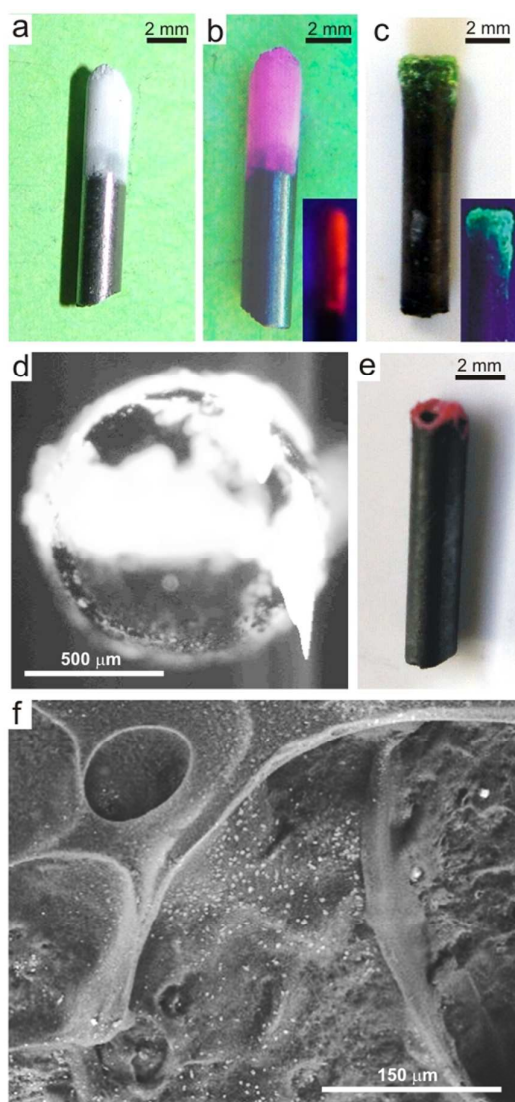
## Supporting information

### INDIRECT BIPOLAR ELECTRODEPOSITION

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#### Entrapping compounds in the deposits

As the deposited amorphous silica and titanate layers are transparent, entrapping white pigments such as alumina or TiO<sub>2</sub> NPs in these matrixes during the deposition can give a strongly opaque white color, as shown with a titanate matrix obtained by indirect bipolar electrochemistry on a carbon rod in the presence of Al<sub>2</sub>O<sub>3</sub> NPs (Figure SI 1a). It is also straight forward to generate coloured layers by infiltration of a dye, such as rhodamine 101, in these layers (Figure SI 1b).



**Figure SI 1.** Encapsulation in the electrodeposited matrices. a) Optical micrograph of a graphite rod modified by a titanate matrix with simultaneous entrapment of alumina particles using indirect bipolar electrodeposition. b) Optical micrograph of such a modified graphite bar which has been infiltrated by rhodamine 101. Inset: Fluorescence of the object revealed under UV light. c) Optical micrograph of a graphite rod, modified by a silica matrix entrapping fluorescein. Inset: fluorescence of the object revealed under UV light d) Fluorescence micrograph of a sub-millimeter bead modified with silica entrapping TiO<sub>2</sub> NPs and rhodamine 101. e) Optical micrograph of a graphite rod modified with an EDP matrix containing AuNPs. f) SEM picture of the EDP deposit from figure 1e, revealing the presence of the gold particles.

Instead of using a post-deposition infiltration step, the chromophore can be directly trapped inside the matrix during the bipolar electrodeposition as in the case of Figure SI 1c where fluorescein has been entrapped in a silica layer. Insets of Figures SI 1b and SI 1c show the corresponding fluorescence of the modified extremities, revealed under a UV lamp ( $\lambda_{\text{ex}} = 254 \text{ nm}$ ). In Figure SI 1d, a fluorescence micrograph of a glassy carbon bead modified by a silica matrix, entrapping TiO<sub>2</sub> pigments, and infiltrated by rhodamine 101 shows that this concept can be used to design microstructured Janus objects with one fluorescent moiety. Even if the fluorescent area is clearly localised only on one half of the bead, some parts in this area do not show luminescence. This inhomogeneity is due to cracks present in the silica matrix, as discussed in the manuscript.

Finally, AuNPs were encapsulated in EDP by depositing the polymer from a mixture containing AuNPs synthesized by the Turkevich method (see experimental section for protocol and Figure SI 2 for characterization). An example is shown in Figure SI 1e, where the red color at the extremity of the rod is attributed to the plasmon absorption of the AuNPs incorporated in the matrix. AuNP aggregates located at the outer surface of the matrix are observable by SEM, as illustrated in Figure SI 1f. These experiments

demonstrate the utility of the IBED process for encapsulation purposes and open the way for the synthesis of a wide family of anisotropically-colored and fluorescent Janus particles, which may be of interest for example as pixels in electronic paper or for biosensing technologies.

## Experimental Details

### Chemicals

All chemicals were used as received. Solutions were prepared using milliQ water (resistivity = 18 M $\Omega$  cm), absolute ethanol (Sigma Aldrich) or 99.9 % methanol (Sigma Aldrich). Gold(III) chloride trihydrate (> 99 %), methyltrimethoxysilane (MTMOS, > 98 %), citric acid trisodium salt (99 %), fluorescein sodium salt, rhodamine 101, titanium(IV) tetra isopropoxide (TTIP, 97 %), tetramethyl ammonium hydroxide pentahydrate (TMAOH, > 95 %), universal indicator solution pH 3-10 and titanium(IV) oxide (anatase, < 25 nm, 99.7 %) were purchased from Sigma-Aldrich. Tetraethylorthosilicate (TEOS, 98 %), agar powder and sodium chloride (99.5 %) were purchased from Acros. Nickel powder (spherical, APS 5 - 15 micron 99.5 %) and glassy carbon powder (spherical, 630 - 1000 micron, type 2) were purchased from Alfa Aesar. Hydrochloric acid solution, 0.1 M was purchased from VWR. Resydrol AY498w/35WA was purchased from Cytech Austria GmbH. BASF coating FT 23-0510 EDP was purchased from BASF. Alumina powder (micropolish, 0.05 micron) was purchased from Buehler.

### Material

Cation-exchange membranes were supplied by NCBE. Feeder electrodes were platinum plates. Carbon-doped polycarbonate sheets were provided from Bayer AG. Carbon graphite rods were extracted from pencils (Stabilo opera 285 2B). Scanning electron microscopy (SEM) characterization was performed using a Hitachi TM-1000. Fluorescence microscopy was performed on a Olympus BXFM-ILHSPU microscope equipped with a Hamamatsu EM-CCD digital camera. X-ray diffraction (XRD) patterns were collected on a PANalytical X'pert MPD Bragg-Brentano  $\theta$ - $\theta$  geometry diffractometer equipped with a secondary monochromator over an angular range of  $2\theta = 20$ - $80^\circ$ . The acquisition lasted for 6 h 55 min. The Cu-K $\alpha$  radiation was generated at 40 KV and 40 mA ( $\lambda = 0.15418$  nm). The samples were collected on sample holders made of aluminum alloy and flattened with a piece of glass. Transmission electron microscopy was achieved using, Formvar/carbon 200 mesh Cu grids (Agar Scientific) that were observed with a FEI Technai 12 equipped with an Orius SC1000 uMPx (GATAN) camera. Photographs were taken using a Sony Cyber-shot camera.

### Power supplies and cells

Different power supplies and cell configurations were used for this work. A number is attributed to each of them in order to simplify protocol descriptions.

Power supply 1 : Sodilec DC power supply, SDL

Power supply 2 : Consort E 862 (6000 V - 150 mA)

Cell 1: Plastic cell without membranes. The outer electrodes are separated by 2.5 cm. The reaction compartment volume is ~ 2.5 mL.

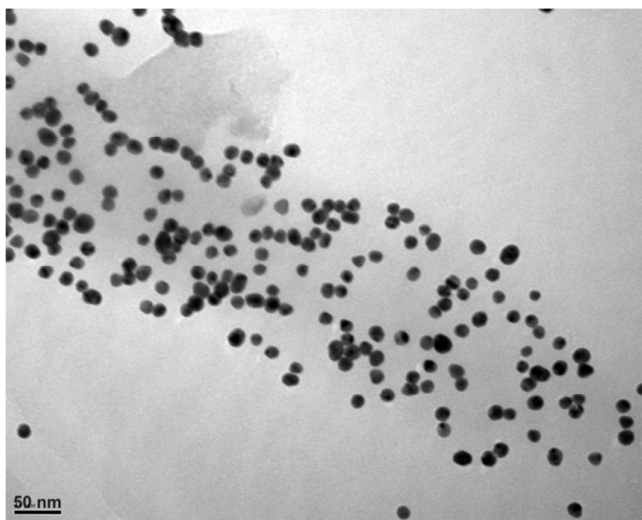
Cell 2: PDMS cell with two membranes (spaced by 2 cm). The outer electrodes are separated by 2.8 cm. The reaction compartment volume is ~ 2 mL.

Cell 3: PDMS cell with two membranes (spaced by 2 cm). The outer electrodes are separated by 2.5 cm. The reaction compartment volume is ~ 2 mL.

Cell 4: Plexiglass cell with two membranes. The separators are spaced by 1 cm and the outer electrodes are separated by 2 cm. The reaction compartment volume is ~ 3 mL.

### Gold nanoparticle (AuNPs) synthesis and characterization

AuNPs were synthesized following the Turkevich protocol. 50 mL of an aqueous solution of 0.5 mM HAuCl<sub>4</sub> was heated in an Erlenmeyer flask under magnetic stirring. When boiling is reached, 0.7 mL of an aqueous solution of 0.1 M sodium citrate was added to the mixture. After a few minutes the color changed from purple to red indicating the presence of metal gold nanocolloids. When a stable color was obtained, the solution was cooled down to room temperature. A suspension droplet was placed on the TEM grid and was sucked from below with a paper tissue. The grid was then rinsed three times with milliQ water following the same procedure. As it is shown by Figure SI 2, TEM imaging revealed roughly spherical AuNPs with sizes ranging from 12 nm to 22 nm.



**Figure SI 2.** TEM micrograph of citrate-stabilized AuNPs.

#### **Bath preparations**

##### **Silica sols**

##### **TEOS-based sol**

The sol composed of 1 g of TEOS, 6 mL of EtOH, 6 mL of an aqueous solution of 0.1 M NaNO<sub>3</sub> and 72  $\mu$ L of 0.1 M HCl was stirred for few hours, and was directly used for IBED.

##### **MTMOS-based sol**

The sol composed of 1 g of MTMOS, 10 mL of MeOH, 10 mL of an aqueous solution of 0.1 M NaNO<sub>3</sub> and 120  $\mu$ L of 0.1 M HCl was stirred for a few hours, and was directly used for IBED.

##### **Titanate sol**

0.355 g of TTIP was added to 25 mL milliQ water. TTIP hydrolysis instantaneously induced the formation of white precipitates. 0.453 g of TMAOH was then added to the mixture. The solution was sonicated for 30 min and stirred during several hours until becoming fully transparent and then used for IBED.

#### **Electrophoretic deposition paint (EDP) bath**

Prior to the experiment, Resydrol and BASF coating FT 23-0510 EDPs were diluted ten times with milliQ water. For cathodic deposition of BASF coating FT 23-0510, hydroquinone (5mM) was added to the bath. Actually, in this way the oxidation reaction is facilitated by decreasing the necessary anodic potential from 1.23V vs SHE (water oxidation) to 0.7V vs SHE (hydroquinone oxidation to benzoquinone). Therefore the overall potential that has to be applied between the two feeder electrodes will be lower.

#### **Observation of pH variations around a bipolar electrode**

The disk-shaped bipolar electrode was cut from a carbon-doped polycarbonate sheet. Cell 1 was filled with 25 mM NaCl aqueous solution and 5 droplets of universal pH indicator. The bipolar electrode was then positioned at the cell bottom and 22 V were imposed between the electrodes using power supply 1.

#### **Bipolar electrodeposition on spherical glassy carbon particles**

In these experiments, the deposition baths and a few beads were placed at the bottom of the reaction compartment of cell 2. Electrode compartments were filled with water. 300 V during 40 s, 400 V during 1 min, 600 V and 200 V during 1 min 30 and 600 V during 20 s were imposed using power supply 2 for the modification with TEOS, MTMOS, titanate and EDP, respectively. After the modification the beads were carefully taken out with tweezers and rinsed.

## **Bipolar electrodeposition of entrapping matrices**

### **Titanate/Al<sub>2</sub>O<sub>3</sub> NPs/rhodamine modification on a graphite rod**

1.84 g of alumina NPs was added to 1.5 mL of TiO<sub>2</sub> sol. The mixture was inserted between the membranes of cell 3, and the graphite rod was positioned at the bottom of this compartment. milliQ water was then added to the electrode compartments. 300 V were applied during 2 min using power supply 2. The rod was then removed from the cell and washed with milliQ water. For fluorophore infiltration, the modified bar was dipped three minutes into a solution of 0.5 mL EtOH containing 5 mg of rhodamine 101, removed and washed with water and ethanol.

### **Silica/fluorescein modification on a graphite rod**

A fluorescent solution was prepared by dissolving 3 mg of fluorescein in 1 mL of water. 1 mL of TEOS-based sol and 100  $\mu$ L of the fluorescent solution were introduced in cell 1. The graphite rod was positioned at the bottom of the cell between the electrodes and 22 V were imposed using power supply 1. After the experiment, the rod was removed and washed with water.

### **EDP/AuNPs modification on a graphite rod**

0.2 mL of the AuNPs colloidal solution and 1 mL of the EDP bath was inserted into cell 1. The graphite rod was positioned at the bottom of the cell between the electrodes and 22 V were imposed using power supply 1. After the experiment, the rod was removed and washed with water.

### **Silica/TiO<sub>2</sub>/rhodamine on glassy carbon beads**

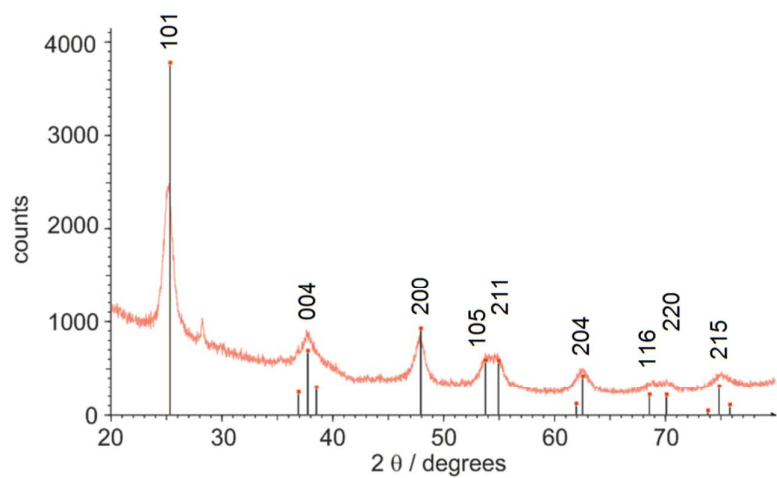
0.2 g of TiO<sub>2</sub> powder was added to 2 mL of the TEOS-based sol. The reaction compartment of Cell 3 was filled with the mixture and a few beads were placed at the bottom of this compartment. The electrode compartments were filled with water and 400 V was imposed using power supply 2. After modification, the beads were carefully taken out with tweezers and rinsed with milliQ water. For the chromophore infiltration, the beads were dipped a few minutes in an ethanol solution containing 0.5 mg of rhodamine 101.

### **Bipolar electrodeposition on micrometer sized metal objects**

First, an agarose-based hydrogel was prepared by mixing 10 mg of agar, 250 mL of Resydrol, 2.25 mL of water and 5 mg of Pt or 9 mg of Ni micropowders in a glass tube. The glass tube was quickly heated at the bottom with a heat gun until the first gas bubbles appeared on the glass walls. The gel was then rapidly cooled down by putting the glass tube under room-temperature water, stirred and sonicated regularly during the cooling process to prevent the particles from agglomeration during the gelling process. When room temperature was reached, the gel was inserted into the reaction compartment of cell 4. Ethanol cooled for 1 min in liquid nitrogen was then added to the electrode compartments. Voltages of 2 kV (for Pt particles) or 2.5 kV (for Ni particles) were imposed for one minute with power supply 2. After modification, the gel was removed from the reaction compartment, inserted in an Erlenmeyer flask and diluted with 50 mL of milliQ water. It was then heated from below with a heat gun until bubbles appeared on the glass walls and particles settled at the bottom of the flask. The hot mixture is then centrifuged at 3000 rpm for 2 minutes. After centrifugation, almost all the supernatant is taken out and the beads are re-dispersed in 50 mL milliQ water, sonicated and centrifuged again for 2 minutes at the same speed. The modified particles were finally dispersed in a small volume of water for conservation.

### **Titanate calcination and TiO<sub>2</sub> crystal structure characterization**

In order to collect as much powder as possible for the XRD analysis, the bipolar electrodeposition was carried out as previously described on ~ 1 cm long carbon-doped polycarbonate sheets with cell 2, imposing 22 V with power supply 1 during 12 min. The corresponding deposits were collected from two modified sheets by scratching and were calcinated at 450 °C during 4 hours before characterization by XRD analysis. Figure SI 3 presents the obtained diffractogram. The characteristic TiO<sub>2</sub> anatase peaks are present demonstrating the crystal structure. A control experiment was also performed with an unmodified polycarbonate sheet revealing only the small unassigned peak at  $2\theta = 28^\circ$  which is directly coming from the substrate.



**Figure SI3.** XRD diffraction spectrum of  $\text{TiO}_2$  after calcination. The positions of characteristic anatase peaks are indicated by lines.