PRELIMINARY ASSESSMENT ON THE ELECTROCHEMICAL SYNTHESIS OF 1-D JANUS PARTICLES FOR CHEMICAL SENSING PURPOSES

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Introduction

Fig. a. Different JPs arrangements.

Fig. b. Janus Roman God.

The term Janus Particles (JPs) defines all those particles displaying a dual anisotropic structure (dual nature), in which two parts with distinct characteristics can be distinguished, thus conferring upon them fascinating properties [**Fig. a**]. The name of this particles is referred to the Roman god of gates [**Fig. b**], having two opposite and distinct faces.

Different methods have been used for JPs preparation such as surface coating, biphasic electrified jetting, photo-polymerization in microfluidic channels, polymer self-assembly (1), and bipolar electrochemistry (BPE) (2) [**Fig. c**]. In this research we focus on the electrochemical preparation of Janus like 1-D nanowires (J-NWs), by membrane template electrochemical deposition using track-etched polycarbonate as hard-template (3, 4) [**Fig. d**].

Fig. c. JP obtained in our laboratory by bipolar electrochemistry.

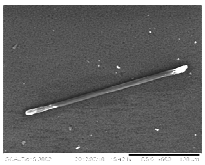
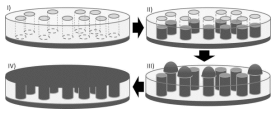


Fig. d. Schematic representation of hard-template deposition.



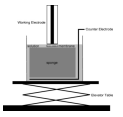
Goals

Synthetic. Develop an experimental procedure suitable for the hard-template synthesis of 1-D Janus particles.

Analytical. Exploit the self-assembly properties of 1-D Janus particles for probing changes in the chemical environment.

Change in chemical environment (pH, redox potential, polarity) → Change in the self assembly of the 1-D Janus particles (*e.g.* , aggregation/disaggregation)

Experimental set up



Polycarbonate membranes (PC, 400 nm pore diameter, SPI-pore) were used as template for J-NWs synthesis. A solution for Cu template deposition was prepared (4).

Before Ag decoration (5), we performed cyclic voltammetric assessments with the aim to individuate the best potential for Ag reduction.

To avoid salt accumulation after Cu and Ag depositions, electrodes were soaked in distillate water. Dichloromethane and ethylic alcohol were used for membrane removal.

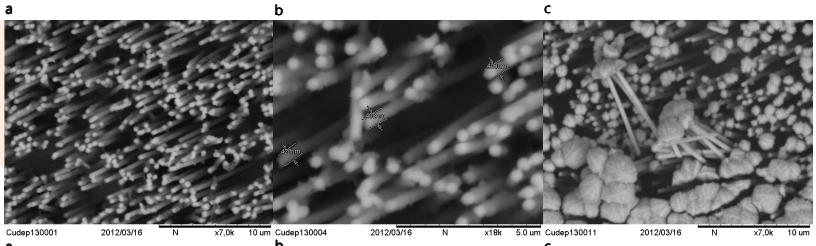
Oxidation process with Oliveira's solution (without $AgNO_3$) facilitates the removing of Cu segment, and allows an easy recovery of Ag nanowires.

After oxidation, the dispersion obtained was filtered in PC membrane (200 nm pore diameter), and SEM observations (TM3000-Hitachi) were performed both on filtered samples and on the surface of the electrodes.

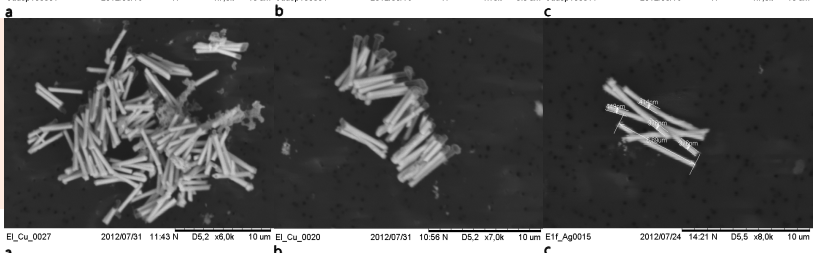
- **Multi Potenziostat Model 1000 A**
  (CH Instruments, Inc.)
  Amperometric method - cathodic current
- **Cu template deposition**
  Working Electrode, Polished Cu disk
  Counter electrode (pseudo-reference), Cu L-shaped sheet
  Cu solution (*Gambirasi et al., 2011*)
  (~pH 1.8) $CuSO_4$ 0.88M
  H_2SO_4 0.55M
  Parameters
  (t=180 s, E=-0.25 V, Smpl int. 0.1 s, sensitivity 0.001 A/V)
- **Ag decoration**
  Working Electrode, Polished Cu disk with Cu nanowires
  Counter electrode (pseudo-reference), Ag L-shaped wire
  Ag solution (*Oliveira et al., 2005*)
  (~pH 11.3) NH_4NO_3 0.1M
  NH_4OH 0.5M
  EDTA Na_2 0.2M
  $AgNO_3$ 0.1M
  Parameters
  (t=300 s, E=-0.50 V, Smpl int. 0.1 s, sensitivity 0.001 A/V)
- **Membrane dissolution**
  Dichloromethane (1/2 - 1 hour)
  Ethylic alcohol (1/2 - 1 hour)
- **Oxidation**
  Working Electrode, Polished Cu
  Counter electrode, Pt
  Reference electrode, Ag L-shaped wire
  from 3600 s, E=-0.15 V, Smpl int. 0.1 s, sensitivity 0.001 A/V
  in the solution proposed by Oliveira without $AgNO_3$

Results

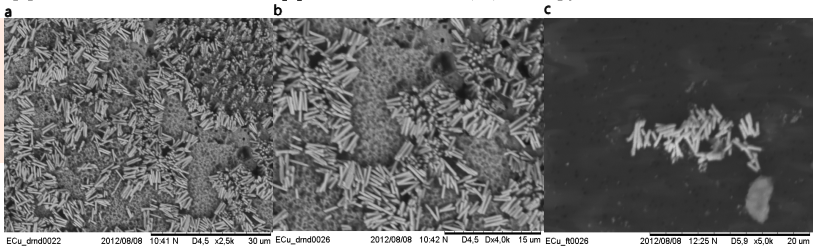
Cu nanowires
Obtained at different time interval (600, 800, 1000, 1200 s). Diameters were estimated by SEM, and were in agreement with the template used (400-450 nm).
a and **b**; 600 s
c; 1200 s



Cu+Ag nanowires
Bi-segmented Janus nanowires are obtained by a dual deposition. Cu can be used as the sacrificial metal removed by oxidation and by NaOH 0.1M soak, while Ag is the portion used for the assembling of J-NWs using or polymer, or organic molecules, or elements. However, as shown in **b**, Cu can be left on site obtaining a Cu-Ag JNW.
a, **b**, and **c**; Cu+Ag and Ag nanowires after their recovering



J-NWs recovery
During the recovery process of Ag nanowires from the surface of the electrode it is important to keep well preserved the morphology of the nanowire synthesized.
a and **b;** residual Ag nanowires on the polished Cu disk
c; Ag nanowires recovered after oxidation and NaOH soak.



Preliminary conclusions and perspectives

- Cu, Ag, and Cu+Ag nanowires are obtained by hard-template deposition. Further assessment are being performed with the aim to improve Ag nanowires recovery.
- Following these preliminary results, the use of polymers will be tested in 1-D JNWs synthesis, *e.g.*, by using Ag on one side and a conductive polymer on the opposite one.
- Preliminary studies on the fabrication of JPs by BPE were conducted in our laboratory with the aim to work with different techniques for JPs synthesis. Promising results were obtained (see Fig. c).
- The objective is to synthesize and characterize from the chemical point of view 1-D JNWs, and make them available for a wide range of analytical applications (environmental, food, clinical, etc.).

References

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