Electrochemical Synthesis and Delivery of Melanin Covered Gold Nanoparticles and Catalytic Activity

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Melanins are an important class of biopolymers which are present in different regions within living organisms[1]. These polymers have very interesting physical features that are closely related to their biological functions. Eumelanin, in particular, possesses fascinating physicochemical properties: a strong, broad UV-band and visible absorption, extremely low radiative quantum yield, anti-oxidant and free radical scavenging ability, and electrical conductivity and photoconductivity in the condensed phase. These biopolymers are able to coordinate a large number of metallic ions, especially iron. The affinity of melanins for metal cations has been studied in relation to melanome cell targeting by different drugs. Recently we have shown that melanin-iron films can be prepared by electrodeposition on Au(111)[2,3] and highly oriented pyrolytic graphite (HOPG)[4,5] surfaces in a controlled way.

The preparation of metallic nanoparticles (NPs) modified with organic, bioorganic or oxide coatings is appealing because of their wide range of potential biological and technological applications in the emerging fields of nanoscience and nanotechnology.[6] In this context, the development of new strategies capable of functionalizing NPs with complex molecular systems by using simple and inexpensive methods is a frontier topic that deserves special attention. Thus, thiol-capped and thiol free gold nanoparticles (AuNPs) 2.7 nm in size spontaneously adsorbed on HOPG have been used as cores for deposition of melanin-iron shells by electrochemical methods. Ultrathin nanostructured melanin films on AuNPs have been prepared by using an electrochemical method.[2-5] Film formation takes place at a noticeable rate at E = –1.0 V (vs. SCE) in a melanin containing 0.1 M NaOH solution for 2 hs. The melanin-iron coated AuNPs were characterized by X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopies, small angle X-ray scattering, scanning tunneling microscopy (STM), atomic force microscopy (AFM), and UV-spectroscopy. Direct deposition on the thiol-capped AuNPs decreases the melanin shell thickness with respect to that formed on thiol-free AuNPs. Thiol electrodesorption results in the delivery of a significant amount of melanin-iron coated AuNPs from the HOPG surface to the electrolyte solution.[7] UV spectra of the solutions and XPS data show that NPs preferentially select dihydroxyindole species or small oligomers from the complex polymer during the electrochemical deposition of melanin. This strategy, which integrates electrochemistry and nanotechnology, could be applied to the preparation of efficient Fe-containing organic catalysts for electrically stimulated delivery devices, in analytical separations, in biosensors, and in nanometer sized magnetic storage devices, among others.

In addition, we have also shown that the iron–melanin coating markedly enhances the catalytic activity of the bare AuNPs for both the hydrogen peroxide electroreduction and hydrogen evolution reaction (HER),[8] see fig. 1. Therefore, this procedure, which combines electrochemistry and nanomaterials, could be applied to the preparation of efficient ‘‘naked’’ AuNP and Fe-organic capped AuNP catalysts.

References

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Figures

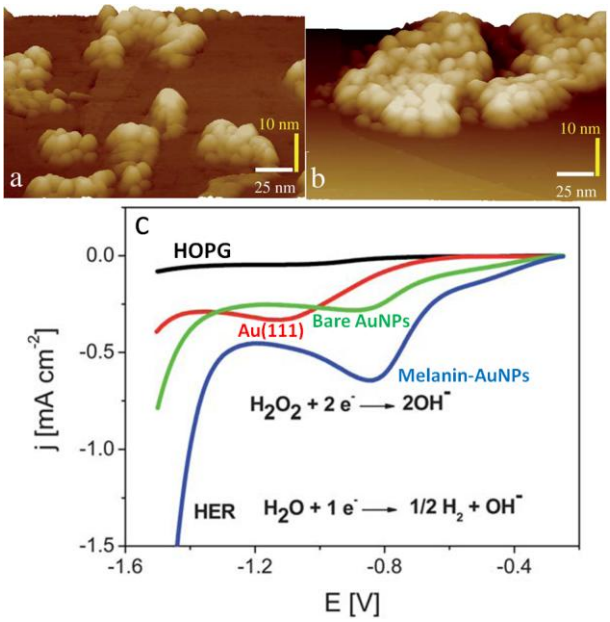

Figure 1. STM images (200 nm x165 nm) of (a) bare AuNPs on HOPG and (b) AuNPs on HOPG after melanin–iron deposition. Cathodic polarization curves recorded at 0.025 V s^{-1} in 4 mM H_2O_2 + 0.1 M NaOH (c).

Acknowledgments

This work was supported by grants CTQ2008-06017/ BQU and ID20100152 from MICINN and ACIISI (Spain), respectively. A. González Orive thanks to ULL for a SEGAI research grant.