Electrocatalytic Nanostructured Surfaces Based on Electrodeposited Dendrimers and Metallic Nanoparticles

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Abstract.
Metallic nanoparticles have busted into research fields as catalysis, sensing and biosensing. They have convulsed to the scientific community including into the research lines followed up till then because their unique properties sensitively dependent on the particle size and shape. Chemical control over the nanoparticle size presents a major challenge to this field.
The synthesis of Au nanoparticles encapsulated within or inter poly(amidoamine) (PAMAM) dendrimers, to be used as electrocatalysts, or their extraction from within dendrimer templates have been studied at length by several authors [1-4]. However, never so far, electrodes modified with dendrimer films have been used for these purposes.
The general targets of this work are the preparation of nanostructurated surfaces with size-controlled metallic nanoparticles and hence the development of new synthetic strategies to prepare electroactive dendritic structures containing functional groups suitable for catalytic applications, supports or templates of metallic nanoparticles in order to develop a new generation of electrochemical sensors and biosensors.
We present in this work two kind of nanostructured surfaces. In the one hand we have prepared surfaces in which the dendrimer film acts as template for the synthesis of AuNPs. In these surfaces the catalyst are the AuNPs or there exists a synergic effect of AuNPs together with te dendrimer active groups. On the other hand we have developed surfaces in which the dendrimer is the catalyst and the films are electrodeposited on a layer of PtNPs. In both cases, we obtain different surfaces with very different applications.
In a similar way than in homogeneous media [5], inter-dendritic Au nanoparticles (figure 1) have been obtained when first or third generation dendrimer modified electrodes were used, while smaller nanoparticles were obtained with fifth generation dendrimer, indicating that intra-dendritic Au nanoparticles are syntethized (figure 2). The AuNps were obtained from a 0.1 mM $HAuCl_4$ solution and subsequent chemical reduction with NaBH4. The ferrocene groups were previously electro oxidized to avoid the direct reduction of Au (III) by the ferrocenyl groups [6]. The formation of AuNps was followed by UV-Vis spectrophotometry by the appearance of the plasmon band at 530 nm in modified ITO electrodes.
The AuDENs modified electrodes were characterized by Ultra High Resolution Scanning Electron Microscopy (UHSEM), which let us estimate the nanoparticles size and to prove that none aggregate is formed in the film. In addition, the particle-size distribution is low and very close to the average particle size, which let us affirm that the dendrimer structure is responsible for the nanoparticles size.This kind of surfaces have shown to be effective catalysts of O_2 tetra electronic reduction and of the dopamine oxidation.
The second kind of surfaces (figure 3) prepared by cycling the Pt electrode in the potassium hexacloroplatinate (IV) solution in the scanning potential range from -0.25 to 0.6 V (vs. SCE) at a scan rate of 50 mV s-1 for 20 cycles [6]. This surfaces have been successfully used as catalyst of electro-oxidation of acetaminophen and as support to the immobilization of enzymes as alcohol dehidrogenase.

References

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Figures

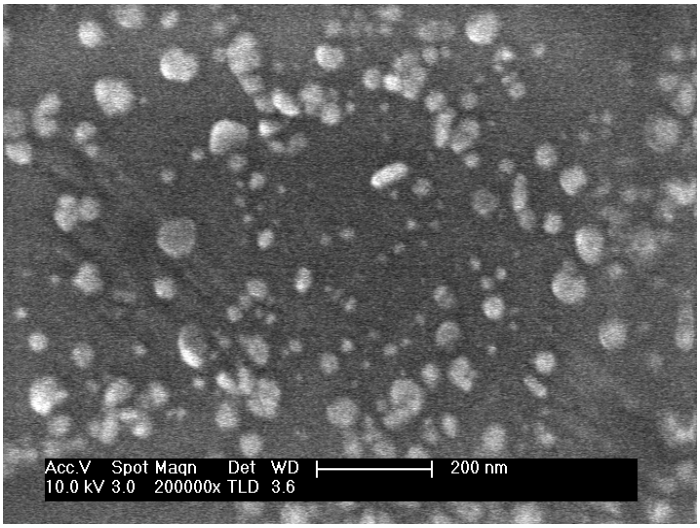

Figure 1. UHSEM micrographs of inter-dendritic AuNPs obtained with a first-generation dendrimer

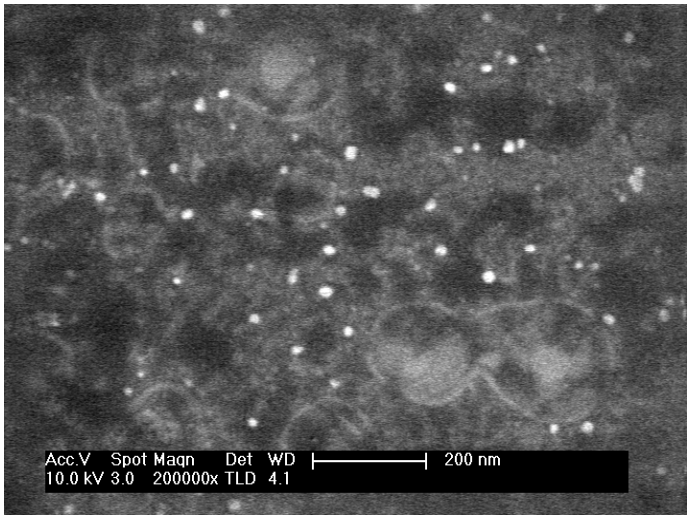

Figure 2. UHSEM micrographs of intra-dendritic AuNPs obtained with a fifth-generation dendrimer

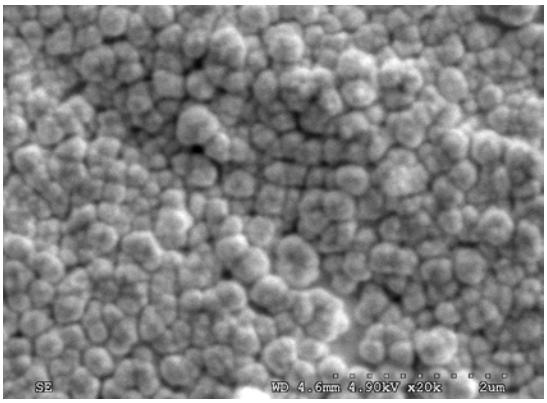

Figure 3. SEM micrograph of a Pt wire modified with PtNPs and a fifth-generation dendrimer