

Catalytic Co and Fe porphyrin/Fe₃O₄ nanoparticles assembled on gold by carbon disulfide



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ABSTRACT

A simple and versatile method for the robust attachment of nanocatalytic assemblies on gold surface is developed. To this purpose, carbon disulfide is used to establish a stable linkage between Au (111) surface and magnetite (Fe₃O₄) nanoparticles, functionalized with metalloporphyrins (Co or Fe) containing carboxylic acids as anchor groups. For comparison purposes the same systems were prepared with gold nanoparticles, which are known to strongly interact with sulfur derivatives. Surface modification is carried out in a one-pot procedure in ethanolic solutions. UV–vis spectra prove the functionalization of the nanoparticles by metalloporphyrins and AFM images reveal the density and size of modified nanoparticles attached to gold by CS₂. The efficiency of the immobilization method is demonstrated by the electrochemical performance of the modified electrodes toward oxygen reduction reaction (ORR) in aqueous acidic medium. Koutecky-Levich plots and rotating ring-disk electrode experiments revealed distinct oxygen reduction mechanisms for the nanostructured Co or Fe porphyrin modified electrodes, with the transfer of two or four electrons to form hydrogen peroxide or water, respectively. The chemical nature, composition and size of nanoparticles clearly influence the ORR behavior. The largest magnetite nanoparticles (ca. 40 nm) exhibit the best catalytic response, either modified with iron or cobalt porphyrins. Additionally, electrodes with metalloporphyrin/Fe₃O₄ nanocatalysts exhibit good stability under acidic conditions. Altogether the results highlight the potentialities of this simple and versatile surface modification for the design of electrocatalytic systems.

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1. Introduction

Porphyrin derivatives are found in a diversity of important biological systems, such as the active site of several proteins [1], and are one of the most attractive classes of molecules to address the catalytic oxygen reduction reaction (ORR) to replace the expensive platinum-based catalysts. The widely reported excellent electrocatalytic properties and stability of porphyrins [2–5] have been encouraging their use. The size of the macrocycle is perfect to coordinate a high number of metal ions [1] and the diversity of this kind of compounds with distinct catalytic properties is due to the variety of central metals as well as the substituent groups in the macrocycle. The ORR is of particular importance in several technological devices, namely on those related with energy conversion and storage. Both the efficiency and power of such systems are governed by the number of electrons transferred in the

oxygen reduction; so, its evaluation is mandatory for a correct management of the performance of such devices. In this context, Fe and Co porphyrins have been extensively explored and commonly Fe porphyrins catalyze the reduction of O₂ through 4 electrons to water, while Co porphyrins promote de ORR via the transfer of 2 electrons to hydrogen peroxide [6].

One of the strategies commonly employed to covalently bind porphyrin molecules to electrode surfaces, including previous work from the group, is the formation of self-assembled monolayers (SAMs) via the derivatization of porphyrins with specific anchor groups: sulfur moieties, e.g. thiols [7], disulfides [8,9], thioctic acids [10], as well as phosphonic acids [11] to extend the immobilization to oxidized surfaces [12]. Other approaches involved the preparation of SAMs containing imidazole-terminated adsorbates which bind covalently to a series of metalloporphyrins [13], or covalent attachment of metalloporphyrins to dimercaptoalkane modified gold electrodes [14].

It is well known that physical and chemical properties of nanomaterials, such as metallic (e.g. Au, Pt, Pd) [15–18] and metal oxide (M_xFe_{3-x}O₄; M = Fe, Cu, Co, Mn) [19] nanoparticles (NPs) or carbon nanotubes (single and multi-wall) [20] play a critical role in

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ORR. For instance, nanostructured gold electrodes [21,22] can be catalytically active toward O_2 reduction, in contrast to flat Au (111) orientations, through the formation of H_2O_2 by a two-electron process at low overpotentials, provided the particle size is in the nanometer range [23]. Benefits arise when the catalytic properties of metalloporphyrins are conjugated with nanomaterials [2,24]. As a result, there is an increase of the catalyst amount on the electrode surface as well as an improvement on the electron transfer reaction, both factors relevant in electrocatalysis [2,22]. This behavior has been clearly demonstrated, for example, for 3D arrangement of gold nanoparticles (AuNPs) functionalized with cobalt porphyrins, prepared by layer-by-layer method [3,25,26], infrared light irradiation [27], and also by electrostatic adsorption [28]. More recently, it has been shown that a metalloporphyrin could enhance the catalytic activity of carbon-supported transition metal (Co, Ni or Fe) oxide nanoparticles [29]. Additionally, it is also recognized that bare iron oxide nanoparticles (Fe_3O_4 NPs) have high chemical activity and are easily oxidized in air. Therefore, proper surface coatings and effective protection strategies must be developed to keep the stability of magnetic iron oxide nanoparticles, especially in acid medium. The methodologies include organic coatings, such as small molecules, surfactants, polymers or biomolecules, or covering with an inorganic shell (e.g. silica or metallic compounds), which stabilizes and may facilitate nanoparticle functionalization [30].

In previous studies, we have described a simple methodology to bio-functionalize gold electrodes through the one-step reaction between AuNPs, carbon disulfide and amine groups, including small molecules (e.g. epinephrine, tryptophan), enzymes (glucose oxidase) [31] and also protein A for immunosensor surface development [32]. The purpose of the present work is to extend the capabilities of carbon disulfide to assemble porphyrin functionalized Fe_3O_4 nanoparticles with different sizes on Au (111), for the construction of electrocatalytic interfaces for ORR. Gold nanoparticles were also used in this work to validate the immobilization methodology through sulfur linkages. The distinctiveness here reported is the use of a simple and versatile one-pot reaction to readily create tridimensional assemblies of noble metal and non-noble metallic nanoparticles, functionalized with bio-inspired metalloporphyrins (Fig. 1). The attachment of nanoparticles *via* CS_2 is expected to occur as proposed in our previous work [31], in which one of the sulfur atoms is anchored to the nanomaterial and the other to the Au surface, as illustrated in Fig. 1.

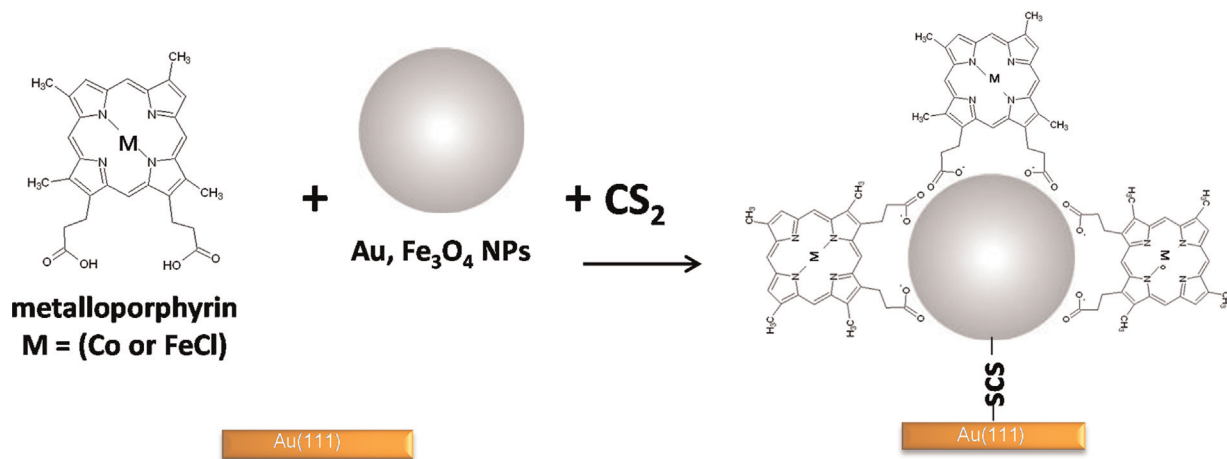


Fig. 1. Schematic illustration of functionalized nanoparticles with a metalloporphyrin containing terminal carboxylic acid groups, attached on Au (111) surface by CS_2 . For simplicity only one CS_2 molecule is represented, although due to the spontaneity of the method more molecules could be adsorbed to the nanoparticle along with metalloporphyrins.

2. Experimental

2.1. Chemicals

Carbon disulfide (Acros Organics), $H AuCl_4$, sodium citrate (Alfa Aesar), $NaBH_4$ (Merck, p.a.), sulfuric acid (Panreac), iron chloride, $FeCl_3 \cdot 6H_2O$ (Sigma–Aldrich), iron sulfate, $FeSO_4 \cdot 7H_2O$ (Merck), ammonia solution (25%, Scharlau), hydrochloric acid (37%, Merck) and absolute ethanol (Riedel-de Haën) were all analytical grade and used without further purification. Phosphate buffer solution was prepared with 8.0 mM Na_2HPO_4 , 1.14 mM KH_2PO_4 , 138 mM, NaCl, 2.7 mM KCl (pH = 7.4) and ultrapure Milli-Q water. Ultra-pure water was obtained from a Milli-Q A10 Gradient purification system (18 M Ω cm at 25 °C) and used to prepare all the aqueous solutions. Cobalt (II) porphyrin (CoP) was especially synthesized according to a reported procedure [33]. Fe(III) deuteroporphyrin IX chloride (FeP) was acquired in Cymit Quimica.

2.2. Gold electrodes

Thin layer gold films (200 nm) deposited on borosilicate glass with a pre-layer of chromium (2–4 nm) from Arrandee™ have been used. The surface was cleaned with *piranha* solution (3:1 mixture (v/v) of $H_2SO_4:H_2O_2$), rinsed with ultra-pure water and ethanol and flame annealed, leading to a predominant (111) crystallographic orientation and a surface roughness of 1.2. The morphological characterization of bare gold surfaces has been previously described [34].

A rotating Au–Au ring-disk electrode with $A_{ring} = 0.062$ cm², $A_{disk} = 0.416$ cm² was also used. These gold surfaces were polished with 5, 1 and 0.3 μ m alumina suspension (Al_2O_3 , Buehler) until a fresh mirror-finish surface was generated and were then rinsed with water. Before each experiment the gold polycrystalline electrodes were characterized in 0.1 M H_2SO_4 by cyclic voltammetry.

2.3. Synthesis of nanoparticles

AuNPs (20 nm) stabilized by citrate ions were synthesized by the Turkevich method [35,36], using 5.0 μ mol $H AuCl_4$ in 19 mL of boiling water and 2 mL of 1.6×10^{-3} M sodium citrate, according to the procedure previously reported [31,37]. AuNPs (ca. 5 nm) also stabilized with citrate ions, have been synthesized as described in

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