Available online at www.sciencedirect.com
ScienceDirect
Journal of Electroanalytical Chemistry 609 (2007) 85–93
Journal of Electroanalytical Chemistry
www.elsevier.com/locate/jelechem

Metallic and bimetallic Cu/Pt species supported on carbon surfaces by means of substituted phenyl groups

Neus Vilà [a], Maarten Van Brussel [b], Mathieu D'Amours [a], Jan Marwan [a], Claudine Buess-Herman [b], Daniel Bélanger [a,*]

[a] *Département de Chimie, Université du Québec à Montréal, Case Postale 8888, succursale Centre-Ville, Montréal, Québec, Canada H3C 3P8*
[b] *Université Libre de Bruxelles, Service de Chimie Analytique et Chimie des Interfaces, C.P.I. 255, Bld du Triomphe, B-1050, Bruxelles, Belgium*

Received 28 November 2006; received in revised form 31 May 2007; accepted 12 June 2007
Available online 25 July 2007

Abstract

Carbon surfaces were functionalized with metallic species by means of 4-sulfophenyl groups previously grafted on the electrode surface by electrochemical reduction of the corresponding diazonium cations "in situ" generated from the corresponding amine. The functionalization with metallic copper is based on electrostatic interactions between sulfonate groups present on the modified carbon surface and copper(II) cations in aqueous solution and its subsequent chemical or electrochemical reduction to metallic copper. Bimetallic modified electrodes based on Cu/Pt were also obtained by replacement of metallic copper on the carbon surface by immersion of the surface in a K_2PtCl_6 aqueous solution. The amount of copper was estimated by stripping voltammetry in aqueous 0.5 M H_2SO_4 whereas adsorption/desorption of hydrogen was used in the same electrolyte to quantify the platinum present on the carbon surface. The resulting metallic functionalized surfaces were characterized by cyclic voltammetry to determine their activity for the electrochemical reduction of nitrate and the hydrogen evolution reaction (HER).

Keywords: Diazonium; Metal; Sulfophenyl groups; In situ generated diazonium; Bimetallic metal displacement reaction; Copper; Platinum

1. Introduction

Bimetallic particles are important materials because they often display properties that are quite different from those of the individual metals. Such materials are of fundamental interest and technological importance due to their applications in catalysis since for several chemical processes it is crucial to have a bifunctional effect [1–6]. For instance, binary PtRu system is the most efficient anode electrocatalyst for methanol oxidation. In this electrocatalyst, Ru is thought to act as an oxygen source to avoid CO poisoning on Pt [7]. As a second example, it has been shown that PdCu particles are good catalysts for the chemical and electrochemical reduction of nitrate. Palladium alone does not show any activity whereas the addition of Cu to this metal promotes the chemical reduction of nitrate with hydrogen as reductant [8]. Thus, it is important to develop novel procedures for the preparation of bimetallic catalysts.

In a recent report, a new metal deposition method was disclosed for the deposition of a submonolayer of Pt, Pd or Ag on Au (1 1 1) surfaces [9]. In this procedure, a Cu adlayer on Au (1 1 1) is used as template for the deposition of these metals which occurred by spontaneous oxidation of Cu by more noble metal ions, which are reduced and simultaneously deposited on Au. In order to control the size, stability and solubility, dendrimers can be used as templates for hosting metal nanoparticles due to the ability of their cavities to trap guest molecules. The synthesis of dendrimer encapsulated bimetallic nanoparticles (Ag/Cu, Au/Cu, Pd/Cu and Pt/Cu) was also described by partial displacement reaction if less than a stoichiometric amount of the noble metal is used leading to the desired

* Corresponding author.
E-mail address: belanger.daniel@uqam.ca (D. Bélanger).

0022-0728/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2007.06.026

composition of the nanoparticle [10]. The preparation of dendrimer encapsulated bimetallic nanoparticles by either a co-complexation method of two different metals followed by a single reduction step or a sequential loading method were also reported by these authors. Redox displacement reactions have also been used to prepare the bimetallic sulfides of Pb–Cd and Zn–Cd [11] and Co–Pt core-shell bimetallic nanoparticles by the reaction of a Pt salt with Co nanoparticles [12]. The first example of a galvanic synthesis of bimetallic nanoparticles using reactions of thiolate monolayer protected metal clusters (MPC) was reported by Murray and coworkers [13] studying the exchange reaction of dodecylthiolate monolayer protected metal (Ag, Pd, Cu) clusters with the more noble metal thiolate complexes $Au[SCH_2(C_6H_4)C(CH_3)_3]$ and $Pd[S(CH_2)_{11}(CH_3)_2]$. The use of carbon nanotubes (CNTs) as templates to immobilize nanoparticles has been also described [14]. CNT's are especially attractive as supports for heterogeneous catalysis due to their appropriate physical properties, high electrical conductivity, high surface area and their size and hollow geometry. A variety of electrochemical, chemical and physical methods have been already described for their functionalization with metals. The modification of CNT's with a monolayer of 4-aminobenzene covalently attached by the electrochemical reduction of the corresponding diazonium salt was used for the immobilization of palladium nanoparticles via electrostatic interactions between aminobenzene protonated groups and the palladium complex, $[PdCl_6]^{2-}$ [14a]. Their functionalization with sulfonic acid was used also as a means to facilitate the deposition of platinum on the CNT surface [14b]. After removal of the organic groups by chemical reduction at high temperature the small platinum nanoparticles obtained were in contact with the carbon paper. On the other hand, the formation of metallic particles supported on a substituted phenyl modified glassy carbon electrode was also recently reported [15–17]. The procedure based on electrostatic interactions involves the adsorption of metallic ionic species at the phenyl modified carbon electrode which bears functional groups that allow the binding of these ions either electrostatically or through metal–ligand bond formation. Later on, they are electrochemically [15] or chemically [16,17] reduced to form metal particles such as Pt, [15–17] Ag, [15] Cu and Ru [16,17].

In this sense, the immobilization of metallic particles on solid surfaces using molecular layers as templates is an interesting approach which can be useful to prevent the agglomeration leading to new materials with interesting properties and that may have several applications as sensors, biosensors or catalysts. Many efforts have been done recently to develop a range of strategies based on electrostatic interactions [18–26], biomolecular recognition [27–29] and covalent coupling[18,30–34]. By varying the surface density of ionic sites which can be used as binding sites for metallic ions it may be possible to control the density and size of metal particles as well as to prevent the agglomeration of metal particles at the electrode surface [35].

In the present work, we investigate the formation of Cu and Cu/Pt species on a 4-sulfophenyl modified carbon electrode by using a method based on the replacement of Cu by Pt [9]. The electrocatalytic activity of the resulting modified electrode was evaluated by cyclic voltammetry selecting chemical reactions for which only either Cu or Pt is a good catalyst. The composition of the metal-loaded electrodes was quantified by stripping voltammetry to estimate the amount of copper on the carbon surface as well as by integration of the hydrogen adsorption/desorption waves to determine the amount of platinum. X-ray photoelectron spectroscopy was also used to further confirm the presence of the grafted groups and metallic species at the electrode surface.

2. Experimental

2.1. Chemicals

Potassium ferricyanide, potassium ferrocyanide, potassium chloride, potassium hydroxide 4-aminobenzenesulfonic acid used for diazonium salt synthesis, sodium nitrite, sodium nitrate, copper(II) sulfate pentahydrate and potassium hexachloroplatinate(IV), sodium borohydride were used as received from Aldrich. Concentrated sulfuric and hydrochloric acids (Fisher) were used as received.

2.2. Electrode preparation and modification

Glassy carbon working electrodes were from Bioanalytical Systems Inc. (Model MF-2012; diameter = 3 mm). Carbon paper electrodes ($0.5 \times 0.5 \times 0.025$ (thickness) cm) were prepared from a carbon paper with 0.45 g cm^{-3} density. The carbon paper (Spectracorp., #2050A) was cleaned and ultrasonicated in Nanopure water (18.0 MΩ cm) for 15 min and after was dried during 12 h under vacuum. A copper wire was used for the electrical contact made with Ag epoxy (Dynaloy, #325) and isolated using an epoxy resin (Epoxy-patch, Dexter Corporation). Platinum gauze of large surface area was used as a counter electrode, which was cleaned by flame annealing and rinsed with Nanopure water before each experiment. All potential measurements were measured and quoted vs. an Ag/AgCl reference electrode (saturated KCl). Prior to the electrochemical derivatization the glassy carbon surface was cleaned by polishing with 1 μm and 0.05 μm alumina slurries. After polishing the electrode was washed and ultrasonicated 5 min in Nanopure water. Following the method previously described [36] the diazonium cations were generated *in situ* from the corresponding amine. Firstly, two equivalents of $NaNO_2$ were added to a solution containing 5 mM of amine and 0.5 M HCl under stirring at room temperature. The mixture was reacting for 5 min before derivatization of the carbon surface. The grafting of the organic layer was carried out by applying −0.6 V for 240 s. After electrochemical derivatization, the surface was rinsed and