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Size control and electrocatalytic properties of chemically synthesized platinum nanoparticles grown on functionalised HOPG

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A method for the *in situ* preparation of Pt nanoparticles of controlled size based on the modification of highly oriented pyrolytic graphite (HOPG) with aminophenyl groups employing diazonium chemistry is demonstrated. It is shown that full chemical reduction of an Ar–NO_2 grafted surface is achieved with aqueous Sn(II). The formation of aminophenyl groups was established by chemical reaction with 1,2-benzoquinone followed by electrochemical detection of the bound quinone using square wave voltammetry. The oxidation state of nitrogen was confirmed by XPS. Platinum nanoparticles were prepared chemically by the attachment of Pt(II) on the Ar–NH_2 modified electrodes followed by reduction with $NaBH_4$. This resulted in the formation of Pt nuclei that could be further grown. The surfaces formed were characterized by TEM, XRD and XPS. The dependence on particle size of the electro-oxidation of CO and methanol in 0.5 M H_2SO_4 was studied for three different nanoparticle sizes, 2.0, 2.7 and 4.0 nm. It is demonstrated that reactivity for these reactions decreases with decreasing particle size. The difficulties in comparing particle sizes calculated from XRD data with those from TEM are discussed.

1. Introduction

Metal nanoparticles containing a few to thousands of atoms have recently been extensively investigated due to their unusual properties [1–3] in particular, since their surface catalytic properties differ considerably from those of the bulk metal or of single-crystals [4,5]. Platinum is an important catalyst for many chemical and electrochemical reactions including oxygen reduction, hydrogen oxidation, methanol oxidation and hydrogenations [6–9]. Practical applications, for instance, in fuel cell electrodes, invariably require particles in the nanometer size regime and their small dimensions leads to differences in reactivity due to imperfections, corners and steps and importantly, changes in the energy of interaction of reaction intermediates with the metal due to the dependence of the electronic structure of the metal nanoparticles on size [10]. It is not surprising, therefore that the catalytic activity of precious metals has been found to depend on size [11–18].

In spite of the many applications of metal nanoparticles, the influence of particle size on electrochemical reactivity is still not fully understood, mainly because of the experimental difficulties in ensuring uniform and controlled sizes and geometries. The attachment or growth of these nanoparticles in good electrical contact with a well-defined inert conducting support constitutes, therefore, a key requirement for understanding their electrocatalytic behaviour. Pt nanoparticles have been attached to electrodes employing different approaches, e.g., using nanoparticles prepared by colloidal chemistry methods, thermal reduction with H_2 of precious metal salts dispersed on an electrode surface, electrodeposition and coordination of a precious metal ion to an appropriate ligand bound to the electrode surface followed by its electrochemical or chemical reduction.

The advantage of using previously synthesized nanoparticles is that their preparation is uncoupled from their attachment to the electrode surface. Citrate stabilized Pt nanoparticles adsorbed on Au electrodes has been used in this way but the stability of electrodes thus prepared is limited to 4–8 potential cycles [19]. Another preparation method involves the adsorption of previously prepared particles on to a previously oxidized carbon surface that has been oxidized to ensure stability of the attached material [20,21]. Oxidation produces surface carboxylic, quinoid, ketonic and/or hydroxylic groups, which act as anchoring points. However, the exact nature and number of oxygen containing functionalities formed under these conditions are difficult to control and corrosion of the carbon surface is often observed, leading to unwanted large background currents in electrochemical experiments. In the case of well-organized layered materials such as HOPG, oxidation at high potentials also leads to severe surface disruption and the

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formation of blisters [22,23]. Surface corrosion can even be intensified and catalysed by the presence of Pt [24].

Although it is possible to support Pt nanoparticles of specific size by controlled chemical attachment [25] or by electrophoresis of colloidal dispersions [26], the ligands required to stabilize the metal dispersion can inhibit electrocatalytic activity. This is particularly important for polymer-stabilized nanoparticles for which the elimination of the stabilizing polymer is difficult even after treatment with O_2 plasma when the particles are adsorbed from their micellar solution [27]. In spite of this, Pt nanoparticles can be cleaned after attachment to the electrode surface by adsorption of CO followed by oxidation [28]. The adsorption of CO is sufficiently strong to displace stabilizing polymers and other impurities from the surface but it is not possible, however, to ascertain that this procedure is quantitative. Nevertheless, this technique is extremely useful in providing a surface cleaning method that is unlikely to lead to large morphological changes. Electrochemical deposition from dilute metal salt solutions has also been used to obtain size-controlled Pt nanoparticles by controlling the electrodeposition parameters [29,30]. Pt nanoparticles of different sizes have also been prepared by spreading H_2PtCl_6 on GC or HOPG surfaces, drying and then reducing with hydrogen at 250 °C [11,31], size control could be achieved by varying the loading with Pt(VI). A similar preparation has also been used to obtain dispersed Pt particles on carbon powders [17,32] that, although very useful for the spectroscopic study of adsorbed intermediates [32], are not very well suited for the study of the kinetics of electron transfer reactions due to large capacitative charging currents and redox processes at carbon surface groups.

The strategy of binding a metal ion to a functionalised surface followed by its subsequent reduction has been employed for the situ synthesis of metal nanoparticles attached to the electrode [33]. Liu et al. [34] prepared an amino-terminated HOPG surface by first functionalizing the surface by reduction of the diazonium salts of 4-amino nitrobenzene followed by its reduction. $PtCl_6^{2-}$ was attached to the $ArNH_2$ termination and then reduced electrochemically. Kolbe et al. [35,36] showed that a sandwich metal|organic|metal structure could be constructed by forming SAMs of 4-mercaptopyridine, then coordinating Pd(II) to it and finally reducing electrochemically the attached Pd ions. This technique results in the growth of a two-dimensional metallic overlayer and provides a means of establishing good molecular contacts to metals. In addition, repetition of this procedure resulted in the growth of uniform two-dimensional layers. The use of a thiol SAM for cluster growth for electrocatalytic investigations, however, presents problems due to the possibility of contamination and poisoning of the electrocatalytic particles by sulfur containing species. A similar strategy has been used to decorate carbon nanotubes with Pt and Pd nanoparticles by functionalization with arene $-NH_2$ or SO_3H terminations employing diazonium chemistry followed by reaction with Pt(II) or Pd(II) followed by electrochemical [37] or chemical reduction (hydrogen at 600 °C) [38] of the bound precious metal ion. Similarly to studies with carbon powder, it is not easy to derive kinetic information from three-dimensional electrodes such as these. Crooks et al. [39–42], Chen et al. [43] and Xie et al. [44] incorporated Pt clusters in dendrimers by covalent attachment of Pt(II) ions to the N groups within the dendrimer organic matrix followed by their chemical reduction. Cluster size could be controlled by increasing the number of ions attached within the dendrimer. The metal particles within the dendrimer were found to be in electrical communication with the electrode surface [39] as shown by the observation of oxygen reduction currents for electrodes modified by adsorbing the dendrimer-nanoparticle composite. Although these systems are of considerable interest, the position of the metal centres with respect to the electrode surface is undefined. This introduces a degree of uncertainty in the measured rates of electron transfer reactions due to the strong dependence of electron transfer rate with distance to the electrode surface and in particular, due to the non-aqueous environment in which the nanoparticles are present.

To avoid the problems described above for establishing a robust technique for studying the dependence of electrocatalytic reaction rate on particle size, a modification strategy based on the covalent attachment of aryl groups onto an HOPG surface by the electrochemical reduction of diazonium compounds [45–49] has been employed. This is a versatile and reliable way for creating functionalized monolayers as support for the synthesis of Pt nanoparticles. *p*-Aminobenzene was chosen as the linker due to the known strong interaction of the amino group with platinum. The method employed follows from the previous work of Liu [34], Kolbe [36] and Crooks [39] but uses a sequential nucleation and growth strategy to control the size of electrocatalytic Pt nanoparticles attached in a well-defined position with respect to the electrode surface. Importantly, the high value of the single molecule conductance of a linker of similar structure has been previously demonstrated [50] thus ensuring the absence of artefacts due to the presence of the bridging linker between the metal particles and the electrode surface. The aim of this work was to investigate, employing the approach described above, the possibility of observing size effects in the technologically important CO and methanol oxidation reactions.

The paper is divided in three sections. Firstly, we describe the preparation and characterization of an amino-terminated HOPG surface onto which Pt(II) can be coordinated; secondly, the formation and characterization of Pt nanoparticles on this film is described and finally, the size dependence of their electrocatalytic properties is presented.

2. Experimental section

2.1. Materials

Potassium chloride (BDH, AnalaR), tetrabutylammonium tetrafluoroborate (Aldrich, 99%), 1,2-dihydroxide benzene (Fluka, puriss), methanol (BDH, AnalaR), potassium tetrachloroplatinate(II) (Aldrich, 99.9+%), sodium dihydrogenphosphate (Aldrich, 99.999%), 4-nitrobenzenediazonium tetrafluoroborate (Fluka, Purum), sodium borohydride (BDH, 98%), highly oriented pyrolytic graphite (HOPG, ZYH grade, Agar Scientific, with a mosaic spread of 3.5 ± 1.5°), glassy carbon (GC) rod, 4 mm diameter, type 2, (Alfa Acer), hydrochloric acid (Riedel-Dehaën, extrapure), Kalrez O-rings (DuPont, supplied by E-A-P International Ltd.), sulfuric acid (Aldrich, 99.999%), acetonitrile (ACN BDH, Gradient grade) and tin(II) chloride (BDH, AnalaR) were used as received. All aqueous solutions were prepared with Milli-Q® water (Millipore system).

2.2. Electrode modification with p-aminobenzene

The electrode modification strategy aimed at obtaining an $Ar-NH_2$ terminated surface to use as support for Pt nanoparticles to take advantage of the strong interaction between Pt and aminobenzene [51]. In addition, it was desirable to employ a molecular linker showing good electrical conductance, such as the phenyl group [50]. This had the dual advantage of providing not only conductivity but also the required diazonium functionalization chemistry. A schematic diagram of the electrochemical cell employed is shown in Fig. 1. A 0.28 cm^2 circular area of the HOPG surface bounded by a Kalrez O-ring was exposed to the electrolyte. The surface of this electrode was renewed by peeling with adhesive tape at least twice before each experiment [23]. The measurements to assess the technique for the determination of surface amino