Journal of Electroanalytical Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Synthesis of Au clusters-redox centre hybrids by diazonium chemistry employing double layer charged gold nanoparticles

Humaira Razzaq[a,b], Rumana Qureshi[b], Laura Cabo-Fernandez[a], David J. Schiffrin[a,*]

[a] Chemistry Department, University of Liverpool, L69 7ZD, United Kingdom
[b] Chemistry Department, Quaid-i-Azam University, Islamabad 45320, Pakistan

ARTICLE INFO

Keywords:
Gold nanoparticles
Quantised double layer charging
Fast Fourier Transform nanoparticle charging analysis
Diazonium functionalisation, anthrahaquinone electrochemistry
Monolayer protected nanoparticle synthesis

ABSTRACT

The experimental conditions in the two-phase synthesis of hexanethiolate gold monolayer-protected clusters (C6-Au) have been investigated by varying the thiolation and reduction times to give particles with an average core diameter of 1.66 nm and a capacitance of 0.54–0.59 aF. These clusters were further functionalised with anthraquinone by reaction between the diazonium derivative of 1-amino anthraquinone and electrochemically or chemically charged nanoparticles. Cyclic voltammetry and differential pulse voltammetry measurements demonstrate functionalisation by the redox couple and the presence of quantised double layer (QDL) charging events at the gold core. The feasibility of using a dispersion of charged nanoparticles as reagents for driving a diazotisation reaction to attach redox ligands is demonstrated.

1. Introduction

Monolayer protected clusters (MPC) have attracted a great deal of interest[1] due to their many possible applications, for example, in plasmonic photothermal cancer therapy [2], for allowing high conductance across molecular wires in long range electron transfer reactions to access redox centres [3,4] and in biological and chemical sensing [5] These require, however, achieving great stability of the hybrid metal-chemically attached ligand structures. Thiols have been extensively employed for this purpose but it is only recently that we are beginning to understand the structure of thiolated nanoclusters, in particular the nature of bonding between thiols and gold, and the importance, in this respect, of Au—Au bonds [6]. Other functionalisation approaches have been extensively explored and one of the most promising employs the reductive attachment of an aryldiazonium cation leading to the formation of a metal-carbon bond [7,8]. In the case of gold, the greater stability of the Au—C over that of the Au—S bond has been experimentally demonstrated [9].

A significant result from the work of McDermott et al. [9] was the observation that octadecanethiol, in contrast to its behaviour for replacing other attached thiols, was unable to fully displace a monolayer of organic moieties bound to the Au surface by diazonium chemistry, thus demonstrating the greater strength of the Au—C bond. More recent work with nanoporous gold confirms this preferential stability [10]. These results are in agreement with quantum chemical calculations that indicate a higher bond energy for C—Au than for S—Au bonds, of the order of 0.4 eV [11], a result that has been recently confirmed [12]. Diazonium chemistry has been successfully employed for the functionalisation of nanoparticles by spontaneous reduction reaction with metal particles [13], by two phase reduction of Au(III) [14] and by direct reaction in solution of citrate stabilised Au nanoparticles with a diazonium compound [15]. In addition to good stability, functionalisation through the formation of Au—C bonds offers a wide availability of the amine precursors employed for the synthesis of the required diazonium compounds.

The attachment of functional groups based on diazonium chemistry offers additional synthetic possibilities for surface functionalisation, in particular, as described in the present work, for the incorporation of strongly bound redox group within a thiol functionalised nanoparticle surface. In a series of important original reports, Murray et al. [1] recognised that monolayer protected clusters could be regarded as dispersed nanoelectrodes. Importantly, due to their small core size and hence, small electrical capacitance, these particles display quantised double layer (QDL) charging behaviour in electrochemical experiments related to discrete charging events [16]. Using this property, the present work attempted to control, in a rational way, the number of organic residues attached per nanoparticles by reacting a pre-charged dispersion of particles with a diazonium compound.

The paper is divided in two sections. The dependence of average size of hexanethiol protected nanoparticles precursor on reaction conditions is described first and then a redox marker, in this case an anthraquinone molecule, was incorporated by reaction of their charged

* Corresponding author.
E-mail address: d.j.schiffrin@liverpool.ac.uk (D.J. Schiffrin).

http://dx.doi.org/10.1016/j.jelechem.2017.05.016
Received 28 March 2017; Received in revised form 8 May 2017; Accepted 11 May 2017

dispersion with the corresponding diazonium compound.

2. Experimental

Full experimental details are given in the Supplementary information section.

2.1. Preparation of hexanethiol monolayer protected clusters (C6-Au)

The synthesis followed a literature protocol [17]. Briefly, a solution of $HAuCl_4{\cdot}3H_2O$ in Milli-Q® water (5.18×10^{-3} mol, 160 ml) was added to a toluene solution of TOABr (0.02 mol, 160 ml; TOA = tetraoctyl ammonium) with vigorous stirring. After 40 min, the water phase was discarded and 1-hexanethiol (0.016 mol, 1:3 Au(III):RSH molar ratio) was added to the organic phase. The reaction between Au (III) and the thiol was allowed to proceed for different times, from 30 min to 6 h, to determine the influence of the formation of the Au(I)-thiol polymer on particle size and monodispersity. A freshly prepared aqueous solution of $NaBH_4$ (6.74×10^{-2} mol, 160 ml, 1:13 molar ratio of Au:$NaBH_4$) was then rapidly added to the mixture at 0 °C with vigorous stirring. The solution turned black immediately and the reaction mixture was left with stirring for 15 to 30 min for the different preparative conditions tested. The phases were separated, the organic phase extensively cleaned with water and then toluene removed by rotatory-evaporation ($T \leq 30$ °C). The black residue was re-suspended in absolute ethanol (160 ml), sonicated and left to settle overnight. The solution was then filtered through a sintered disc filter funnel and the filtrate transferred to a round-bottomed flask to remove the ethanol under vacuum. The nanoparticles were then suspended in approximately 160 ml of acetonitrile, sonicated for 15 min and left standing overnight. Finally, the capped particles were filtered and washed with acetonitrile. The reason for only using the ethanol soluble fraction was to restrict the subsequent analysis to the low molecular weight fraction of the preparation. Precipitation of the reaction mixture with solvents such as acetone leads to a range of sizes that do not display well defined QDL behaviour, a central point of the present work, requiring further fractionation.

2.2. Attachment of anthraquinone to nanoparticles

To simplify notation, we have indicated throughout the text AQ to mean the 1-anthraquinone bonded moiety. Anthraquinone functionalised nanoparticles (AQ-C6-Au) were prepared by reaction of electrochemically or chemically charged nanoparticles with the diazonium derivative of anthraquinone (AQ-N_2^+). C6-Au particles were used as a stable starting material for the attachment of AQ by reducing AQ-N_2^+ at the nanoparticle surface according to [7]:

$$RN_2^+ + e^- \rightarrow R^{\cdot} + N_2 \quad (1)$$

followed by the reductive coupling of the radical (AQ· in this case) at the Au nanoparticle surface:

$$R^{\cdot} + e^- + Au_n \rightarrow R - Au_n \quad (2)$$

The reduction of the N_2^+ group must be carried out adjacent to the metal surface to be functionalised. This reaction was achieved by first injecting electrons into a nanoparticle dispersion followed, in a separate step, by reaction in solution with the diazonium compound.

2.2.1. AQ functionalisation by electrochemical charging

C6-Au particles were further functionalised with anthraquinone employing its diazonium derivative. Two methods for charge injection were employed, direct electrochemical charging and a two phase redox reaction with borohydride as reducing agent in the aqueous phase. A well-defined number of electrons could therefore, be injected in the nanoparticles and used to carry out the surface functionalisation shown in reactions (1)–(2) without the need of applying external potential for reducing the N_2^+ group.

A solution of C6-Au nanoparticles (59 μM in a 2:1 toluene-acetonitrile solvent mixture containing 0.1 M $TBAPF_6$ as base electrolyte) was placed in contact under stirring with an electrode held at a potential of −1 V for approximately 6 h. AQ-N_2^+ (0.2 mM in a 2:1 a toluene-acetonitrile solvent mixture) was then added to the electrolysed nanoparticles in a 3:1 molar ratio (AQ-N_2^+:C6-Au) and the reaction mixture kept under stirring for 12 h. The nanoparticles were then precipitated, filtered and washed with acetonitrile to eliminate the supporting electrolyte and any unreacted AQ-N_2^+. The solid was dried, redispersed in toluene and precipitated with addition of acetonitrile.

2.2.2. AQ functionalisation by two-phase redox charging

A C6-Au nanoparticle dispersion in toluene (59 μM i.e., 5.9 mg in 3 ml) was reduced in a two-phase reaction by mixing it with a 1 mM aqueous solution of $NaBH_4$ for approximately 6 h under continuous stirring. The organic phase was then washed with Milli-Q® water to remove excess of $NaBH_4$. After phase separation, a AQ-N_2^+ solution (0.2 mM in the toluene-acetonitrile solvent mixture) was added to the organic phase in a 3:1 molar ratio (AQ-N_2^+: C6-Au) and the reaction allowed to proceed for 12 h. The nanoparticles were then separated as described above.

2.3. Electrochemical measurements

Electrochemical measurements were performed with an Autolab potentiostat (PGSTAT 10, Eco Chemie B.V., The Netherlands) using the General Purpose Electrochemical System (GPES) software. The gold clusters were dissolved in 0.1 M $TBAPF_6$ in a toluene: acetonitrile (2:1) mixture. A gold electrode embedded in glass (Area = 0.0314 cm^2) and a platinum mesh were used as working and counter electrodes, respectively. The potentials are referred to Ag/AgCl/3 M NaCl. The reference electrode was separated from the main solution by a salt bridge filled with an aqueous solution of 0.1 M TBACl.

3. Results and discussion

3.1. Spectroscopy and TEM results

The UV–vis spectra of the as-synthesised C6-Au and AQ-C6-Au particles are shown in Fig. 1. The 520 nm characteristic plasmon band

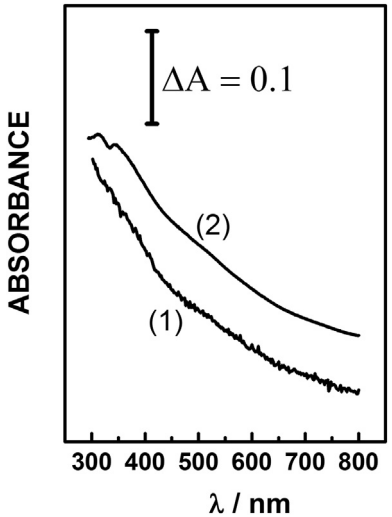

Fig. 1. Comparison of UV–vis spectra in toluene of the as-synthesised C6-Au particles (1) and after functionalisation with AQ employing the two-phase charging method (2). The concentrations were 0.28 μM and for comparison purposes, the absorbance values of the two datasets were normalised at 800 nm. The C6-Au material corresponds to entry 2 in Table 1 (See later). For clarity, the results are offset in the figure.