



Short communication

Electroassisted click chemistry immobilisation of gold nanoparticles on a solid substrate

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ABSTRACT

In this paper a new electrochemical approach for covalent immobilisation of nanoparticles on a solid surface is described. Terminal alkyne modified gold nanoparticles have been deposited on an azide-functionalised glassy carbon surface by electrochemical generation of the Cu(I) catalyst for the Huisgen “click” reaction. The electrochemical catalyst generation offers good control over the process time and the influence of the process time on the surface coverage and the aggregation factor have been investigated. The efficiency of the electroassisted click-chemistry deposition was compared to standard chemical clicking.

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1. Introduction

Gold nanoparticles (AuNPs) can be immobilised on a solid substrate by electrochemical methods such as electrodeposition, electrophoresis or via physical adsorption using techniques such as Langmuir–Blodgett, Langmuir–Schaefer, layer by layer deposition and many other [1]. These methods are based on relatively weak physical interactions, that lead to mechanically fragile deposits. Immobilised AuNPs have found many applications in sensors, molecular electronics, plasmonics, surface enhanced Raman spectroscopy and catalysis [2]. Despite a great number of available immobilisation methods there is still a need for one that allows one to covalently bind gold nanoparticles to a surface in a simple, controlled way. Covalent binding is much stronger than physical adsorption, so the deposits obtained in this way are much more durable. This is especially important for sensor applications where multiple washing steps are frequently applied. The sensing platform needs to be able to withstand these harsh conditions without significant changes.

Click chemistry is a strategy that allows one to form complex chemical structures from simple building blocks using fast, reliable and selective chemical reactions. One of the most frequently utilised click reactions is a Cu(I) catalysed reaction between organic azides and terminal alkyne leading to 1,4 substituted 1,2,3-triazole ring formation. The reaction is known in the literature as the Huisgen reaction. Originally designed for organic synthesis, nowadays it is more and more often

used in nanoengineering and nanomaterial chemistry [3–8]. Click-chemistry was previously used for modification of a gold surface with amine- or carboxylic-terminated compounds to which gold nanoparticles could be electrostatically attached [9]. Recently, click chemistry was employed to immobilise gold nanoparticles on a solid surface [10–13].

In this work gold nanoparticles modified with terminal alkyne groups have been covalently bound to an azide-modified glassy carbon electrode (GCE) surface by electrochemical generation of the Cu(I) catalyst. Electrochemical catalyst generation offers better control over the process time as compared to chemical formation of Cu(I). There are several reports on performing click chemistry on a surface by electrochemical generation of Cu(I) catalyst [14–17]. However, the “electro-click” method has not been used previously for immobilisation of nanoparticles on solid surfaces.

2. Experimental

2.1. Chemicals and materials

4-Azidoaniline hydrochloride, hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), trisodium citrate, copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and KCl were purchased from Sigma-Aldrich. NaNO_2 was purchased from POCH. Hydrochloric acid was purchased from Chempur. 10-Undecyn-1-thiol was purchased from Prochimia. Glassy carbon plates were obtained from HTW. All chemicals were used without any further purification.

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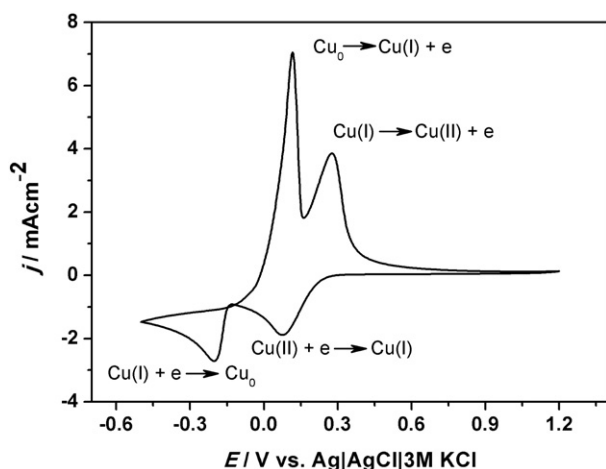


Fig. 1. Cyclic voltammogram of a glassy carbon electrode in 10 mM CuSO_4 , 0.1 M KCl, and a scan rate of 10 mVs^{-1} .

2.2. Synthesis of terminal alkyne modified AuNPs

Gold nanoparticles have been synthesised according to the literature procedure [18]. Briefly, to a 300 ml stirred and boiled solution of HAuCl_4 (0.5 mM) 30 ml of trisodium citrate solution (38.8 mM) was quickly added and boiled until the solution changed colour from yellow to red. The obtained AuNPs with a diameter of c.a. 10 nm were stored at 4°C . Next, the citrate capped AuNPs were further modified with 10-undecyn-1-thiol according to a previously described procedure [10] to achieve a 1% surface ligand-thiol coverage based on the simple geometrical estimate of the number of sites [10].

2.3. Preparation of the azide-modified glassy carbon electrodes

The GCE was polished successively with a sequence of alumina slurry (1, 0.3 and $0.05 \mu\text{m}$) and water on a lapping cloth followed by sonication in ethanol and water for 15 min. Each and dried in a stream of argon. The clean GCE was electrochemically functionalised with azide groups by electrochemical reduction of 4-azidoaniline diazonium cations generated in situ according to a literature procedure [11,19]. This type of surface modification is well known and widely described in the literature [20–23]. A diazonium solution was obtained by adding NaNO_2 (1 mg) to a HCl solution (5 ml, 0.5 M) containing 4-azidoaniline hydrochloride (3 mM) and left in darkness in an ice bath for 40 min. Next, the formed diazonium cations were electrochemically grafted on the GC surface by cycling voltammetry (2 cycles, from 0 V to -0.8 V vs. Ag|AgCl|3 M KCl with 100 mV/s), followed by a washing procedure to remove unbounded species and dried in a stream of argon.

2.4. Procedure of electroassisted deposition of AuNPs on azide-modified GCE

The azide-modified GCE (GCE-N_3) was dipped into the terminal alkyne functionalised AuNPs colloidal suspension enriched with CuSO_4 ($0.25 \mu\text{M}$) and KCl ($3.75 \mu\text{M}$). The $0.25 \mu\text{M}$ concentration of CuSO_4 was chosen because it was the highest CuSO_4 concentration in which the colloidal gold nanoparticle suspension was stable. The supporting electrolyte concentration was decreased compared to what is conventional since too high ionic strength leads to colloidal gold precipitation. Choosing an appropriate deposition suspension composition is a crucial step in the process of electroassisted click chemistry deposition of nanoparticles. A constant potential (-0.12 V vs. Ag|AgCl) was applied to the electrode in order to reduce copper (II) to copper (I). This particular potential has been chosen based on cyclic voltammetry (Fig. 1). After the modification the electrodes were rinsed with water and dried in a stream of argon.

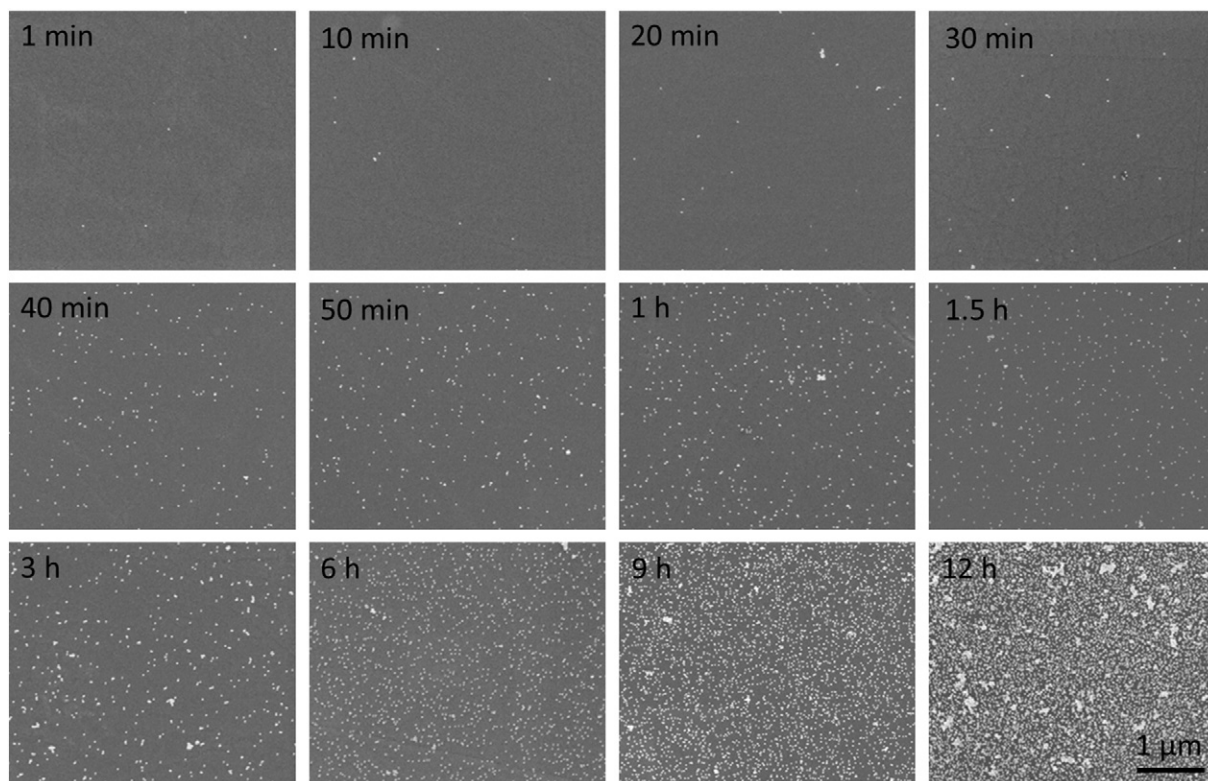


Fig. 2. SEM images of azide modified glassy carbon electrodes decorated with AuNPs by electrochemically assisted click chemistry. Various deposition times.

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