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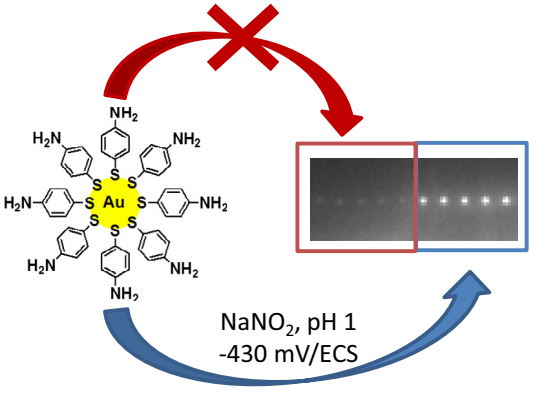
Enhanced chemiluminescence-based detection on gold substrate after electrografting of diazonium precursor-coated gold nanoparticles

Ali Houmed Adabo [a], Rabah Zeggari [b], Nasser Mohamed Saïd [a], Rana Bazzi [a], Céline Elie-Caille [b], Christophe Marquette [c], Matteo Martini [d], Olivier Tillement [d], Pascal Perriat [e], Carole Chaix [f], Wilfrid Boireau [b], Stéphane Roux [a,*]

[a] Institut UTINAM, UMR 6213 CNRS-Université de Franche-Comté, 25030 Besançon Cedex, France
[b] Institut FEMTO-ST, UMR 6174 CNRS-Université de Franche-Comté, 25044 Besançon Cedex, France
[c] Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, UMR 5246 CNRS-Université Lyon 1, 69622 Villeurbanne Cedex, France
[d] Institut Lumière Matière, UMR 5306 CNRS-Université Lyon 1, 69622 Villeurbanne Cedex, France
[e] Matériaux Ingénierie et Science, UMR 5510 CNRS-INSA de Lyon, 69621 Villeurbanne Cedex, France
[f] Institut des Sciences Analytiques, UMR 5280 CNRS-Université de Lyon 1, 69100 Villeurbanne Cedex, France

GRAPHICAL ABSTRACT



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ABSTRACT

Since it was demonstrated that nanostructured surfaces are more efficient for the detection based on the specific capture of analytes, there is a real need to develop strategies for grafting nanoparticles onto flat surfaces. Among the different routes for the functionalization of a surface, the reduction of diazonium salts appears very attractive for the covalent immobilization of nanoparticles because this method does not require a pre-treatment of the surface. For achieving this goal, gold nanoparticles coated by precursor of diazonium salts were synthesized by reduction of gold salt in presence of mercaptoaniline. These mercaptoaniline-coated gold nanoparticles (Au@MA) were successfully immobilized onto various conducting substrates (indium tin oxide (ITO), glassy carbon (GC) and gold electrodes with flat terraces)

Abbreviations: AFM, Atomic Force Microscopy; a.u., arbitrary units; Au@MA, mercaptoaniline-coated gold nanoparticles; CCD, charge-coupled device; GC, glassy carbon; HCl_{aq}, hydrochloric acid; ICP-MS, Inductively Coupled Plasma-Mass Spectrometry; ITO, indium tin oxide; MA, mercaptoaniline; MWCO, molecular weight cut-off; P5, tri-thiolated pentapeptide modified with a biotin molecule at its N-terminal end; PBS, Phosphate Buffer Saline; SAP, streptavidin–peroxidase; SCE, saturated calomel electrode; TEM, Transmission Electron Microscopy; TOAB, tetraoctylammonium bromide; UV, ultraviolet.

* Corresponding author.
E-mail addresses: alialfred@hotmail.com (A. Houmed Adabo), rabah.zeggari@femto-st.fr (R. Zeggari), said.nasser_mohamed@univ-fcomte.fr (N. Mohamed Saïd), rana.bazzi@univ-fcomte.fr (R. Bazzi), celine.caille@femto-st.fr (C. Elie-Caille), christophe.marquette@univ-lyon1.fr (C. Marquette), matteo.martini@univ-lyon1.fr (M. Martini), olivier.tillement@univ-lyon1.fr (O. Tillement), pascal.perriat@insa-lyon.fr (P. Perriat), carole.chaix-bauvais@univ-lyon1.fr (C. Chaix), wilfrid.boireau@femto-st.fr (W. Boireau), stephane.roux@univ-fcomte.fr (S. Roux).

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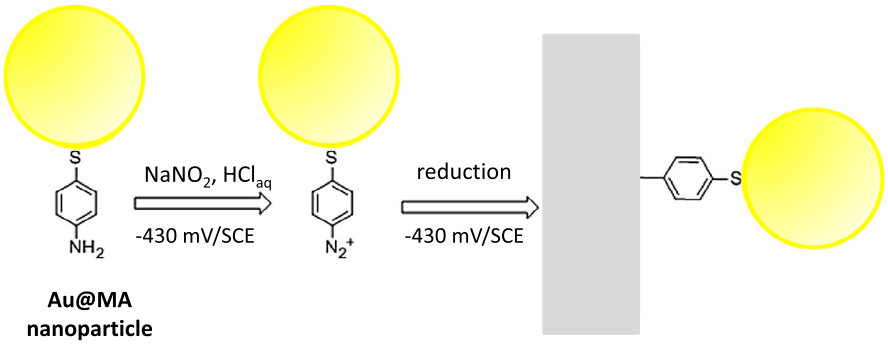
after addition of sodium nitrite at fixed potential. When applied onto the gold electrodes, such a grafting strategy led to an obvious enhancement of the luminescence of luminol used for the biodetection.

1. Introduction

The detection of traces of toxic elements, pathogenic microorganisms or disease biomarkers are of tremendous interest in order to adopt as quickly as possible the most suited behavior facing to the risk of workers and population contamination, epidemic or exponential growth of tumors [1–4]. There is therefore a real need to render sensors more efficient. The nanostructuration constitutes an interesting route for improving the sensor sensitivity [3–5]. Indeed, the resulting surface area increase leads to a higher amount of the probes onto the sensor surface. Moreover the corrugation favors the interaction between the capture probes and the targets due to a better suited orientation of the probes. In the case of gold surface, the corrugation is also accompanied by a catalytic effect which leads to enhance the chemiluminescence of luminol [6–8]. This was confirmed by the study of Cui *et al.* on the gold nanoparticles self-assembled electrodes which exhibit electrocatalytic property and redox activity to the luminol electroluminescence system [9]. The (electro)chemiluminescence enhancement observed on these surfaces can be related to the fact that free and especially agglomerated gold nanoparticles exert a catalytic effect on the oxidation of the luminol [10–15]. Such an enhancement can be exploited for lowering the detection threshold since (electro)chemiluminescence of luminol is commonly used for biosensing [16–18]. The nanostructuration of a surface can be achieved by different physical and chemical routes. In the case of gold, silver and gold–silver alloy surface, it has been demonstrated that thermal treatment is appropriate for generating roughness which is at the origin of an enhancement of luminol luminescence by catalytic effect in the case of gold [6,7]. However the most intuitive strategy for obtaining nanostructured surface lies in the immobilization of nanoparticles onto flat surfaces [19–25]. Moreover this strategy can be applied to a larger variety of substrates in contrast to thermal treatment. In many cases, this requires the derivatization of the substrates in order to ensure a strong grafting of the nanoparticles. The research groups of Pinson and Belanger opened the door to a versatile and robust method for derivatizing a large range of substrates (metal (noble but also oxidizable metals), glassy carbon, cellulose (paper, wood, and wool)...) [26–32]. They demonstrated that a thin layer of organic molecules can be covalently bound to a substrate after reduction of functional aryldiazonium salts. In the case of aryldiazonium salt with a substituent in para position, this strategy allows the long-lasting immobilization of various functional groups onto a substrate which can confer novel properties to the materials or can be used as anchoring sites for a further functionalization. The surface chemistry can be therefore accurately tailored in order to immobilize nanoparticles. Negatively charged gold nanoparticles (citrate coated gold nanoparticles) were successfully grafted via electrostatic interactions onto gold after several chemical modification steps of a thin film deposited through electrochemical reduction of hydroxyethylaryldiazonium salts [33,34]. However, the chemical modification of the aryl layer can be avoided when nanoparticles and film carry complementary reactive groups. Magnetic iron oxide nanoparticles with amine functions can be indeed immobilized by electrostatic interactions with carboxylate groups present in the organic film obtained by electrochemical reduction of 4-carboxyphenyldiazonium tetrafluoroborate [35]. In order to avoid the surface derivatization step of the substrate, the use of nanoparticles coated by diazonium precursors can be envisaged for directly grafting nanoparticles onto a naked substrate. Despite the advantages that this direct strategy could afford, the studies devoted to the one-step grafting of nanoparticles on bare substrate through electrochemical reduction of diazonium-coated nanoparticles are rare. In previous study, diazonium functionalized silica particles (~150 nm) were covalently attached onto a naked gold surface [36]. The electrochemical reduction of diazonium moieties led to the formation of particle clusters onto gold surface. Although a precise control of the surface functionalization is not achieved, this pioneering study is very encouraging because it obviously demonstrated that the use of diazonium functionalized particles can be covalently attached on bare substrate. Owing to their attractive properties (tunable optical and catalytic properties), the covalent attachment of gold nanoparticles via the electrochemical reduction of diazonium cation appears as a promising route for tailoring sensitive surface of sensor. For achieving this, we developed the synthesis of mercaptoaniline-coated gold nanoparticles (Au@MA) and an electrochemical method for their covalent attachment on glassy carbon (GC), indium tin oxide (ITO) and gold electrodes. The aromatic primary amine of mercaptoaniline is indeed expected to behave as a diazonium precursor which can be converted *in situ* using sodium nitrite during the electrochemical step as demonstrated by Belanger *et al.* in the case of the grafting of diaminobenzene molecules (Scheme 1) [37]. Finally the potential



Scheme 1. Electrochemical grafting of Au@MA nanoparticles on a conductive substrate.