Applied Surface Science 362 (2016) 42–48

Contents lists available at ScienceDirect

Applied Surface Science

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

Gold nanoparticles-decorated fluoroalkylsilane nano-assemblies for electrocatalytic applications

Barbara Ballarin[a,*], Davide Barreca[b], Maria Cristina Cassani[a,*], Giorgio Carraro[c], Chiara Maccato[c], Adriana Mignani[d], Dario Lazzari[e,1], Maurizio Bertola[e]

[a] Department of Industrial Chemistry "Toso Montanari", UdR INSTM of Bologna and CIRI MAM, Alma Mater Studiorum – University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy
[b] CNR-IENI and INSTM, Department of Chemistry, Padova University, Via Marzolo 1, 35131 Padova, Italy
[c] Department of Chemistry, Padova University and INSTM, Via Marzolo 1, 35131 Padova, Italy
[d] Center for Industrial Research – Advanced Applications in Mechanical Engineering and Materials Technology (CIRI-MAM), University of Bologna, Viale del Risorgimento 2, 40136 Bologna, Italy
[e] Miteni S.p.A., Località Colombara 91, 36070 Trissino, VI, Italy

ARTICLE INFO

Article history:
Received 10 September 2015
Received in revised form
16 November 2015
Accepted 24 November 2015
Available online 2 December 2015

Keywords:
Fluoroalkylsilanes
Gold nanoparticles
Electrocatalysis
Methanol oxidation

ABSTRACT

Metal/organosilane/oxide sandwich structures were prepared *via* a two-step self-assembly method. First, indium tin oxide (ITO) substrates were functionalized with the following fluoroalkylsilanes (FAS): $R_FC(O)N(H)(CH_2)_3Si(OMe)_3$ (**1**, $R_F = C_5F_{11}$), containing an embedded amide between the perfluoroalkyl chain and the syloxanic moiety, and $R_F(CH_2)_2Si(OEt)_3$ (**2**, $R_F = C_6F_{13}$). Subsequently, Au nanoparticles (Au_{NPs}) introduction in the obtained systems was carried out by controlled immersion into a solution of citrate-stabilized Au_{NPs}. The physico-chemical properties of the target materials were thoroughly investigated by using various complementary techniques. Finally, the application of such systems as catalysts for methanol electro-oxidation under alkaline conditions was investigated, revealing the synergistical role played by FAS and Au_{NPs} in promoting a remarkable electrocatalytic activity.

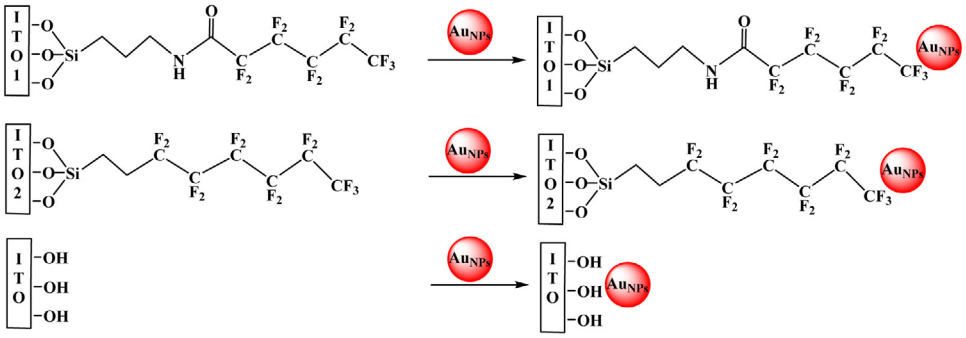
1. Introduction

Gold nanoparticles (Au_{NPs}) have been the subject of several studies due to their size-dependent electronic and optical properties, good conductivity, high biocompatibility, and remarkable catalytic activity [1–3]. These characteristics can be finely tuned as a function of their size distribution and spatial dispersion, which, in turn, are directly dependent on the preparation and processing routes [4–7], as well as to the adopted substrates. In this regard, sandwich structures composed by metal/self-assembled organosilane/oxide have attracted an increasing attention thanks to their possible applications in different fields, encompassing molecular electronics, nanocatalysis and optical sensors [8–10]. In particular, self-assembled monolayers (SAMs) on indium tin oxide (ITO), a transparent and conducting substrate, are of great interest for use in a variety of electronic devices, including heat-reflective coatings, electroluminescent, LCD and plasma displays [11–14]. In this context, fluoroalkylsilane self-assembled monolayers (FSAMs) are extremely attractive candidates for the possibility of tailoring the surface physico-chemical properties such as wettability, biocompatibility and corrosion resistance at molecular level [8,12,15–19]. As a matter of fact, FSAMs contain a well ordered structure with controllable organic functional groups [20], making them suitable for further chemical modification. In this regard, Keil et al. [10,21] have reported the preparation of silver nanoparticles on FSAMs with different fluoroalkyl chain lengths, studying the effect of the latter on nanoparticle assembly. Nevertheless, the bioaccumulation, toxicity and environmental persistence of FSAM containing long perfluorinated alkyl chains (R_F) has boosted the interest toward environmentally safer building blocks with shorter R_F, involving no more than six carbon atoms (R_F with $C < 6$) [22–25].

In line with these issues [23,24], we have recently reported on the preparation of a fluoroalkylsilane-coated ITO system (ITO-1) making use of $R_FC(O)N(H)(CH_2)_3Si(OMe)_3$ (**1**, $R_F = C_5F_{11}$), a fluoroalkylsilane (FAS) containing an embedded amide between the perfluoroalkyl chain and the syloxanic moiety. The presence of the amide group, which promotes intermolecular hydrogen bonding,

* Corresponding authors.
E-mail addresses: barbara.ballarin@unibo.it (B. Ballarin), maria.cassani@unibo.it (M.C. Cassani).
[1] Present address: ICAP-SIRA S.p.A., Via Corridoni 19, 20015 Parabiago, MI, Italy.

http://dx.doi.org/10.1016/j.apsusc.2015.11.219
0169-4332/



Scheme 1. Preparation of **Au_{NPs}/ITO-1**, **Au_{NPs}/ITO-2** and **Au_{NPs}/ITO**.

plays a key role in balancing the lower fluorine content, and can be considered an effective alternative for technological applications in which oil- and water-repellent coatings are requested [26].

The aim of the present work is the investigation of a gold-based transparent amphiphobic conductor obtained by self-assembly of citrate-stabilized Au_{NPs} on ITO-1. The properties of this **Au_{NPs}/ITO-1** structure are investigated in detail, focusing the attention on its catalytic activity in a standard test reaction, *i.e.* methanol oxidation (MEO) in alkaline media [27–31]. Under these conditions, Au_{NPs} generally exhibit a high electrocatalytic activity due to the surface adsorption of oxygen-containing species, such as OH^- ions, possessing a promoting role in electro-oxidation of alcohols [32].

The electrocatalytic behavior of **Au_{NPs}/ITO-1** was also compared with that of **Au_{NPs}/ITO-2**, obtained using $R_F(CH_2)_2Si(OEt)_3$ (**2**, $R_F = C_6F_{13}$), and with that of ITO substrates directly modified with self-assembled Au_{NPs} (**Au_{NPs}/ITO**). To the best of our knowledge, only a few studies on the preparation of metal nanoparticles/FSAM/oxide structures are available in the literature up to date [10,21,33,34], and this work provides the first example on the use of FAS **1**, containing an amide group, for the target applications.

Information on the surface chemical composition and morphology have been obtained by means of X-ray photoelectron spectroscopy (XPS), field emission-scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM). Optical absorption features, contact angles (CAs), as well as the surface free energy and the resistivity to charge transfer (electrochemical impedance spectroscopy measurements, EIS) of the different systems, have been also investigated.

2. Experimental

2.1. Chemicals

The fluoroalkylsilane 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-*N*-[3-(trimethoxysilyl)propyl]hexanamide) (**1**) was produced in-house by Miteni S.p.A. [26,35]. $HAuCl_4 \cdot 3H_2O$ was prepared according to the literature [36]. Diiodomethane, $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, KNO_3, trisodium citrate ($Na_3C_6H_5O_7$) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyltriethoxysilane (**2**) were purchased from Sigma-Aldrich® and used as received. Ultrapure water purified with the Milli-Q plus system (Millipore Co., resistivity >18 MΩ cm) was used in all cases.

2.2. Sample preparation

ITO glasses were purchased from Optical Filters Ltd., UK (surface resistivity = 12 Ω cm). Prior to modification, ITO glass slides (size = 0.7 cm × 2 cm) were cleaned in warm acetone for 5 min, rinsed in 1:1 Milli-Q water/isopropanol under sonication for 30 min, thoroughly washed with Milli-Q water and finally dried under a nitrogen flow.

2.3. Au_{NPs}/FSAM-ITO preparation

The preparation route of the target systems is presented in Scheme 1.

Briefly, pre-cleaned ITO slides were immersed into a 5% (v/v) solution of the chosen fluoroalkylsilane (**1** or **2**) in isopropanol for 24 h in air at room temperature, followed by rinsing with pure isopropanol and heating at 100 °C for 10 min [37–41]. Subsequently, the ITO-1 and ITO-2 were placed in vials containing 5 mL of freshly prepared Au_{NPs} solution for 30 min, and then thoroughly rinsed with MilliQ water, dried and stored under nitrogen [39,42,43]. The Au_{NPs} colloidal solution (particle size of 14 ± 4 nm) was obtained by reduction of aqueous $HAuCl_4$ with trisodium citrate (pH 6.0, 1.1 mM) [37]. For comparison, a pristine ITO glass was directly modified with Au_{NPs} following the same route (Fig. 1).

2.4. Instrumentation

XPS analyses were carried out using a Perkin Elmer Φ 5600ci spectrometer at a working pressure lower than 10^{-8} mbar, using a standard AlKα excitation source ($h\nu$ = 1486.6 eV). The spectrometer was calibrated by assigning to the $Au4f_{7/2}$ line the Binding Energy (BE) of 84.0 eV with respect to the Fermi level. Charging correction was carried out by assigning to the adventitious C1s photopeak a BE value of 284.8 eV [44]. The estimated BE standard deviation was ±0.2 eV. After a Shirley-type background subtraction [45], raw spectra were fitted by means of a non-linear least-squares deconvolution program, adopting Gaussian–Lorentzian peak shapes. Atomic percentages were evaluated using Φ V5.4A sensitivity factors. FE-SEM measurements were carried out with

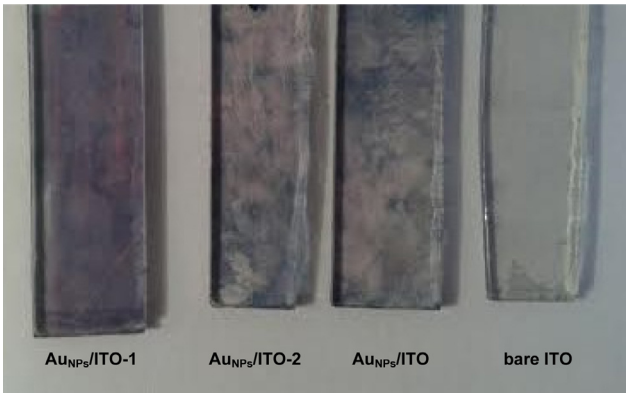


Fig. 1. Digital photographs of **Au_{NPs}/ITO-1**, **Au_{NPs}/ITO-2**, **Au_{NPs}/ITO** and bare ITO.