



Novel methodology for gold nanoparticles deposition on carbon monolith supports



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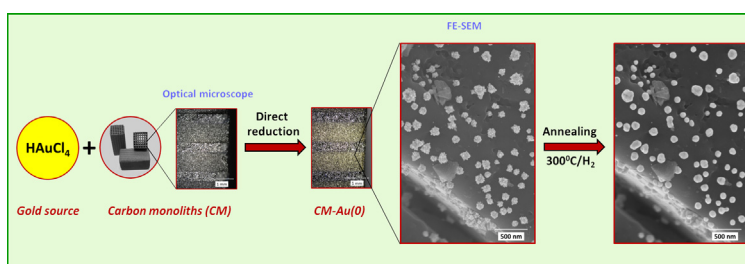
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HIGHLIGHTS

- Gold nanoparticles are deposited onto carbon monoliths.
- Gold is reduced by the own carbon material.
- Two different materials are prepared with different gold concentrations.
- Materials are characterized by different techniques XPS, ICP, SEM-EDX, FE-SEM.
- Heat treatment led to changes in gold particle morphology.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper describes a new methodology for gold nanoparticle deposition onto honeycomb monoliths made exclusively of carbon. Gold nanoparticles were deposited by direct reduction of Au (III) compound by the carbon material in the actual support. Gold solution was forced to pass through the channels of the monolithic support in order to achieve a homogeneous deposition along the channels. After gold deposition, annealing was applied to the materials under a reduction atmosphere, in order to ensure that the gold was in an elemental state (Au⁰) and to achieve good anchoring to the support surface. Two materials with different average sizes for the deposited gold nanoparticles have been developed using this new methodology. These materials were characterized by means of different techniques: X-ray Photoelectron Spectroscopy (particularly to monitor the chemical states of the gold during the annealing process), Inductively Coupled Plasma-Atomic Emission Spectrometry, Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy to control the amount and homogeneity of gold particle deposition along the channels and Field Emission Scanning Electron Microscopy to determine particle size distribution and the area covered by gold.

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1. Introduction

In the last thirty years gold has been found to become active for many reactions [1] when it is stabilized in the form of nanoparticles, increasing the use of gold nanoparticles (GNPs) for a wide variety of reactions, [2,3], and in different applications, such as hydrogen fuel

processing for fuel cells [4] and pollution control in automotive pollution abatement [5]. The activity of these materials has been shown to depend greatly upon both the methods of preparation and the supports on which GNPs are deposited and stabilized. Moreover, gold nanoparticles deposited on structured supports could be used as regenerable sorbent for Hg capture via amalgamation [6,7]. The mechanism of Hg–Au amalgamation [8] and dealumination [9] has been studied under vacuum and ambient conditions [10] in order to be applied for mercury capture from water [11] or flue gas [7]. Therefore gold nanoparticles deposited on structured supports

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could be used as regenerable sorbent for Hg capture in gas streams via amalgamation.

GNPs can be prepared by applying a wide variety of methodologies. One of the best known is the colloidal gold method [12]. In this methodology, a citrate anion acts as a reducing agent for the gold salt and as a protector for the GNPs formed, preventing their aggregation. Recent developments in have led to new methodologies for the preparation of GNPs for glucose oxidation, but the use of protecting and reducing agents such as polyvinylpyrrolidone [13] and polyvinyl alcohol [14], and reducing agents such as NaBH_4 [15], which are harmful for environment, have hindered their application on an industrial scale.

In recent years GNPs have been deposited onto different supports, such as carbon nanotubes [16–18], alumina [11], spherical carbon structures [19], zeolites [20], silica [21] and monolith structures [7]. Monolithic structures have been used for different environmental applications [22] because of they show a very low pressure drop, high surface area to volume ratio and avoid particle entrainment

Direct reduction of the gold precursor can be a solution for GNP deposition onto different carbon structures, avoiding the use of such chemicals as protectors or reducing agents. In this case, GNPs are deposited and stabilized on supports such as carbon nanotubes [17]. Study has also been made into electrochemical gold deposition onto glassy carbon substrates, showing that different deposition conditions can control surface area covered and GNP size [23]. Although direct reduction onto carbonaceous supports has been used for catalytic purposes [24] the novelty of this work is the GNP deposition onto carbon monoliths (MC) to obtain a sorbent for mercury capture that can be regenerated by heating.

In this work, a new methodology to deposit GNPs onto structured MC which are suitable for industrial applications is described. This process is based on the direct reduction of an Au salt on a MC and can be considered a waste free process (without the addition of reducing or protective chemicals). Two different deposition conditions were used to prepare regenerable sorbents for mercury capture which exhibit different gold content and particle size distribution.

Regenerable sorbents based on GNPs retain mercury by amalgamation [7,25] and exhausted sorbents can be regenerated by heating at low temperatures. This process of mercury capturing by amalgamation-deamalgamation has been tested at *pilot scale* (MerCAP) [26]. It consists of a series of gold-coated plates arranged in parallel. In comparison, sorbents described in this work have a very low gold content but a great relationship surface/gold weigh has been achieved because gold is deposited as nanoparticles.

2. Materials and methods

2.1. Support

Raw material used in this work to prepare the support was honeycomb monolith made of polygranular carbon material (NOVACARB), acquired from MAST Carbon International Ltd.

A block of carbon material was cut and smoothed to obtain rectangular prisms with 36 channels (0.8 mm × 0.8 mm channel section), 15 mm length and 7 mm × 7 mm section. These carbon monoliths (MC) became supports for gold deposition.

2.2. Gold deposition

The starting gold solution for material preparation was $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma–Aldrich G4022) dissolved in pure water (Milli-Q, 18 M Ω cm). Different dilutions were prepared in water,

Table 1
Conditions for gold deposition.

Material	Gold concentration (mg Au/l)	Flow time (min)	Flow (ml/h)
MC-Au-1	20	30	225
MC-Au-2	20	12	48

ethanol 96% (Scharlau-ET0013100) and a mixture of both in order to check the influence of liquid medium on gold deposition process.

A Pharmacia Biotech P-1 peristaltic pump was used to force the gold solution to pass through the channels. The gold solution was passed in a two-way flow in order to achieve homogeneous gold deposition along the channels. PTFE tubes were used to connect the pump to the monolith support. This support consisted of two pieces of glass connected to the pump and the gold reservoir, respectively. The monolith was held tightly in silicone stoppers with square windows; those stoppers were coupled to the pieces of glass to anchor the monolith during gold deposition (Figure S1 of Electronic Supplementary Material, ESM). A complete diagram of the device is shown in Figure S2 of ESM.

The variables considered for the deposition process were: liquid medium, gold concentration in solution, injection flow and injection time. The media considered were: water, ethanol, and a mixture (1:1, v/v) of both; the gold concentration was 20 mg Au/l, the injection flows were 48–225 ml/h and the flow times were 12–30 min.

First it was necessary to remove the air occluded inside the MCs. For this purpose, the monoliths were immersed in ethanol/water (1:1, v/v) and sonicated for 10 min. The choice of this liquid medium is explained in the results section.

To evacuate air from the ducts used to inject the gold solution into the monolith channels, the ethanol/water mixture (1:1) was pumped through as a previous step to gold injection.

Two materials were prepared and labeled as MC-Au-1 for material with higher gold concentration and MC-Au-2 for material with lower gold concentrations. A large number of tests were planned combining values in the ranges mentioned for the variables considered. The conditions for the preparation of the two materials with different gold loads are shown in Table 1. This methodology involved the constant passing of fresh gold solution, once it had passed through the support, solution was not used again.

Flow time indicates the time that the gold solution was flowing through the monolith at the indicated flow. The MC-Au-1 material was prepared in a continuous mode where the gold solution was constantly flowing. As previously mentioned, the gold solution flowed in one direction for half of the time, with the solution being pumped in the opposite direction after that. Preparation of the MC-Au-2 material was carried out by 12 steps (every step = 1 min solution flowing + 5 min stop) with gold solution flowing in the same direction during the first 6 steps and changing the flow direction for the next 6 steps.

This procedure was performed in order to provide the best particle distribution, while attempting to avoid concentration differences at both ends of the monolith (higher concentration at the entrance end than at the exit end). Gold solutions were run at flows equal to or higher than 48 ml/h, enabling the fluid inside the channel to be renewed at least 1.5 times/min. Those flow conditions were sufficient to prevent the growth in the size of potential gas bubbles (CO_2) that could limit the movement of liquid through the channels. These bubbles are associated with the process of oxidation of carbon material to CO_2 [27,28].

Once the deposition was completed, distilled water was pumped at 48 ml/h to remove any gold solution inside the monolith until chlorides were no longer detected. The monolith was then dried at 30 °C in a vacuum for 30 min.

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