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SELF-ASSEMBLED GOLD-DENDRIMER COMPOSITE NANOPARTICLES AS SURFACE NANOSTRUCTURING FEATURES

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Various gold-dendrimer nanocomposites were obtained through a simple colloidal chemistry method, using two types of carboxyl-terminated dendrimers, without additional reducing agents, at room temperature. Polyamidoamine dendrimers with simple carboxyl ending groups and with a short tetrafunctional ethylenediamine core have been used, as well as polyamidoamine dendrimers with succinamic acid terminal groups and dodecanediamine tetrafunctional core. The concentration of carboxyl ending groups has been maintained constant, at values of 1mM and, respectively 2mM. Gold nanoparticles obtained using sodium citrate at the same concentration of COO- have been synthesized and used as control. All the so-formed particles were used to generate nanostructured coatings for various substrates.

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1. Introduction

Recently there is an increasing interest and awareness of the use of noble metal nanoparticles in various applications such as sensors, drug delivery and advanced medical applications [1-10]. Various methods of colloidal chemistry have been elaborated for obtaining noble metal nanoparticles, including the use of plant extracts [11-12]. We recently synthesized gold nanoparticles using a citrate-mediated reduction, in order to induce the biomimetic calcification (formation of bone-like apatite) on different substrates, after surface coating with carboxyl-ended self assembled monolayers [2]. Accordingly, the surface of poly(2-hydroxyethyl methacrylate) (PHEMA) has been nanostructured using gold nanoparticles modified with a carboxyl-ended thiol. The so-formed spherical beads have been used to homogeneously coat the polymer surface, leading to a nanostructured topography. In the present study we evaluated the possibility to further use gold nanoparticles in order to nanostructure surfaces obtaining different topographies. Noble metals-dendrimer composite nanoparticles have been obtained in the last 15 years in the presence of dendrimers through already common procedures [1, 13-23]. Dendrimers are well known globular macromolecules with a typical architecture with branches diverging from a central core; the multifunctionality and the monodispersity are among their most important specific features. Therefore, these molecules represent interesting hosts to accommodate, initiate and further guide crystal development inside the internal cages of their tree-like skeleton. Different factors such as the dendrimer type, chemistry, generation number, terminal and internal chemical

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functionality are generally recognized to play decisive roles on the morphology, size, stability and self-assembling propensity of the so-synthesized metal nanoparticles. PAMAM (poly(amidoamine)) dendrimers are extensively researched for the synthesis or stabilization of gold and silver nanoparticles. Metal-dendrimer nanocomposites have been mainly prepared using PAMAM with ethylenediamine (EDA)-core [13, 24] and amine [13, 15, 17, 19, 25], carboxylate [13, 15], thiol [24], and hydroxyl [15] terminal functional groups. To the best of the authors' knowledge, PAMAM succinamic acid (PAMAM-SA) dendrimers with 1,12 - dodecanediamine core have never been used by other groups to prepare gold nanoparticles. We have recently reported such a synthesis method [26]. In this work we compare the nanostructuring potential of composite nanoparticles prepared using gold precursor and PAMAM and PAMAM-SA carboxyl-ended dendrimers. The morphology, crystalinity and self-assembling potential of these materials have been investigated and compared. Gold nanoparticles synthesized using sodium citrate have been used as control nanostructuring units.

2. Experimental

2.1 Materials

Chloroauric acid ($HAuCl_4 \cdot H_2O$) (Sigma-Aldrich, Steinheim, Germany) was used as precursor to obtain gold nanoparticles. Polyamidoamine dendrimers (PAMAM) generations 1.5 and 3.5 and PAMAM-succinamic acid with 1,12-dodecyldiaminododecane core (PAMAM-SA), generations 2 and 4 respectively, have been as received from Sigma-Aldrich (20% methanolic or 10% aqueous solutions). The dendrimers are denoted PAMAM Gi and PAMAM-SA Gi, with i being the generation number. All other chemicals used in this study were from Sigma-Aldrich and used as received. The double distilled water used in this study has been obtained with a GFL 2101-2108 bidistiller apparatus.

2.2 Techniques

2.2.1 Preparation of metal-dendrimer nanoparticles

Dendrimer-gold composites nanoparticles have been prepared using dendrimers, without additional reducing agents and at room temperature. The molar ratio Au(III) /carboxylic groups from the external functional shell of the dendrimers has been kept constant; two such ratios have been used, namely 5:1 and 2.5:1, respectively.

For example, for a molar ratio Au(III)/ carboxyl groups from PAMAM G1.5 of 5, to 2 ml aqueous solution of gold precursor (with a concentration of 5 mM), the corresponding amount of dendrimer methanolic solution has been added under vigorous stirring. The yellow colour of the precursor solution vanished rapidly after the addition of the polymer. This is a piece of evidence for the occurrence of a rapid complexation between the functional groups of the dendrimer and gold. Approximately 20-30 minutes later, the slightly yellow colour of the mixture turns light blue and then dark red / purple. During 24 hours, the colour turns deep purple. Agglomerations become visible after 24 hours and precipitate on the bottom of the synthesis vessel, when stirring is stopped.

By adjusting the ratio metal/carboxyl groups from the two types of dendrimers, different nanoparticles have been obtained and they have been further denoted Au-PAMAM-Gi-j, Au-PAMAM-SA-Gi-j, Au stating for atomic gold, Gi for the generation of the dendrimer and j for the molar ratio between Au(III) and carboxyl groups. Separately, two types of gold nanoparticles denoted further Au-citrate-j (with j molar ratio between Au(III) and carboxyl groups) have been obtained using the method previously reported in [2].

All the syntheses have been repeated in the presence of polymer PHEMA cylindrical scaffolds. PHEMA has been prepared using a radical free polymerization initiated by benzoyl peroxide, as described in [2]. At the end of the reactions, the polymer has been coated by nanoparticles.

2.3 Characterization

UV-vis spectroscopy. The optical properties have been evidenced through UV-VIS spectra recorded using a CINTRA 101 spectrometer. Quartz cells with 1 cm pathway have been used.

Morphological and structural information with respect to the shape, size and eventual assembling or agglomeration of the formed gold-dendrimers nanoparticles has been obtained by *Scanning electron microscopy (SEM)* and *Transmission electron microscopy (TEM)*. SEM analysis was performed using a QUANTA INSPECT F SEM device equipped with a field emission gun (FEG) with 1.2 nm resolution and with an X-ray energy dispersive spectrometer (EDS). *TEM* and high resolution TEM (HR-TEM) analyses have been performed for detailed analysis of morphological features and crystallinity of the colloidal gold. In this respect, 20 µl aqueous-ethanolic solution containing dispersed NPs were dropped directly onto the C-coated cupper grid and allowed to dry in air, for 30 minutes before the measurement.

3. Results and discussion

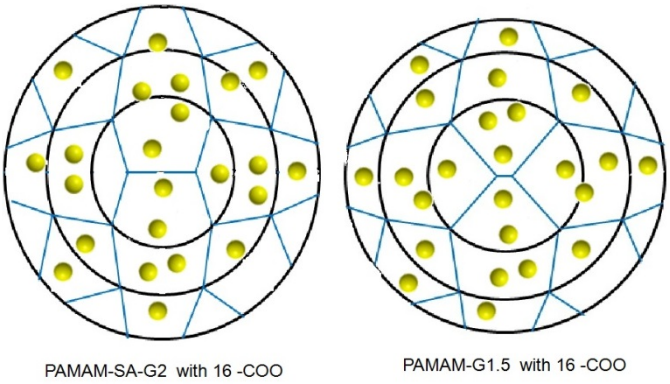
Two types of dendrimers have been used in this study. PAMAM-SA dendrimers have a longer core unit consisting in 1,12-dodecanediamine, when compared to the shorter EDA core of PAMAM. The structural units of the dendrimer branches remain [-CH_2-CH_2-CO-NH-CH_2-CH_2-N-]. Due to the longer core unit, PAMAM-SA molecules used in this work are more open structures, with larger central cages, when compared to the corresponding PAMAM dendrimers. In the present work we describe the synthesis and characterization of gold nanoparticles in the presence of two types of carboxyl-ending dendrimers, PAMAM and PAMAM-SA, in the absence of additional reducing agents, at room temperature. On the other hand, this work demonstrates the potential of such composite nanoparticles to be used as nanostructuring agents for polymer substrates, generating interesting topographies, as further described.

3.1 Obtaining crystalline gold-dendrimer nanocomposites

In the first part of this study, we aimed to prove the formation of gold nanoparticles in the absence of additional reducing agents. Two types of macromolecules, with two generation numbers corresponding to 16 and, respectively 64 carboxyl terminal groups on the external shell, have been utilized from each dendrimer family. The two ratios between the gold precursor and the terminal groups of the dendrimers have been used: 5 and 2.5. The appearance of a deep red colour in all the reaction media was the first piece of evidence for the successful synthesis of gold nanoparticles. However, the color of the colloidal solutions changed in time if stirring was stopped, due to the formation of larger aggregates. These structures can be re-dispersed through vigorous stirring, using ultrasounds. The nanoparticles obtained using citrate are stable in time, in the same conditions; they do not precipitate. UV-Vis spectra have confirmed these facts through the detection of the surface plasmon resonance (SPR) of gold; accordingly, broad bands with maxima in the interval from 520 to 540 nm have been recorded. These are SPR signals indicating the formation of low dimension nanoparticles. These results also indicated that the generation numbers and the concentration of the dendrimers strongly influence the characteristics of the generated nanoparticles. Increasing the dendrimer concentration in the reaction media has been followed by a small blue-shift of the SPR maxima (Table 1). Such behaviour is associated with a decrease of the particle size. Our data confirm similar effects associated with increasing the amount of poly(propylene imine) PPI dendrimers [27-28], or PAMAM with EDA core units and various terminal groups [19, 24]. Furthermore, increasing the generation of the dendrimer has generated broader peaks and a hypsochromic effect of the SPR maxima, also indicating the formation of smaller nanoparticles (see Table 1). This is also considered to be typical UV-Vis feature for the nanoparticles prepared using dendrimers. Broadening of the SPR is considered by Kiang to be an indication for the formation of self-assembled aggregates [29]. No significant difference has been observed between the equivalent members of the two families of dendrimers (with the same number of external functions), PAMAM and PAMAM-SA, despite the different volume of the internal cages of their molecules.

Table 1 Optical properties of the nanoparticles, as recorded through UV-Vis spectra. Characteristics of dendrimer and compositions of the reaction medium are mentioned.

Dendrimer type	Generation number, i	Terminal groups per molecule	Au(III)/COO- molar ratio, j	SPR maximum, nm
PAMAM	1.5	16	5	535
PAMAM	1.5	16	2.5	531
PAMAM	3.5	64	5	532
PAMAM	3.5	64	2.5	530
PAMAM-SA	2	16	5	536
PAMAM-SA	2	16	2.5	531
PAMAM-SA	4	64	5	534
PAMAM-SA	4	64	2.5	531



Scheme 1. Schematic view of dendrimer encapsulation into the two dendrimers with 16 terminal carboxyls from the two dendrimer families: PAMAM-SA G2 and PAMAM G1.5. Circles suggest generation evolution. The differences in the dendrimers' architecture are schematically suggested, with longer core in PAMAM-SA, and shorter terminal branches in PAMAM.

These optical characteristics have been further verified using electron microscopy. TEM and HR-TEM indicated that all the nanoparticles are highly crystalline structures, with nearly spherical shape. Selected area diffraction and HR-TEM analyses have evidenced atomic planes indicating a face-centered cubic (fcc) lattice specific to gold. Typical spacing for adjacent lattice planes of (fcc) gold were identified as follows: 2.36 Å corresponding to (111) planes, 2.04 Å for (200) planes, 1.23 Å corresponding to (311) planes, 1.18 Å corresponding to (220) planes, 1.02 Å corresponding to (400) planes; these results are in perfect agreement with data obtained and reported in a different work [26].

The size differences anticipated by the UV-Vis study have been confirmed by TEM and HR-TEM. As an example, Au-PAMAM-SA-G2-5 nanoparticles had the average dimension 25.01 ± 8.49 nm, while for Au-PAMAM-SA-G2-2.5, the mean values of the diameters are 12.22 ± 7.16 nm [26]. It can be observed that increasing twice the amount of dendrimer has generated a two times decrease of the size of the nanoparticles. Similar results have been obtained for Au-PAMAM-G1.5-j (j=5 and 2.5). In all these four cases, the size of the nanoparticles is higher than that of the dendrimer used.

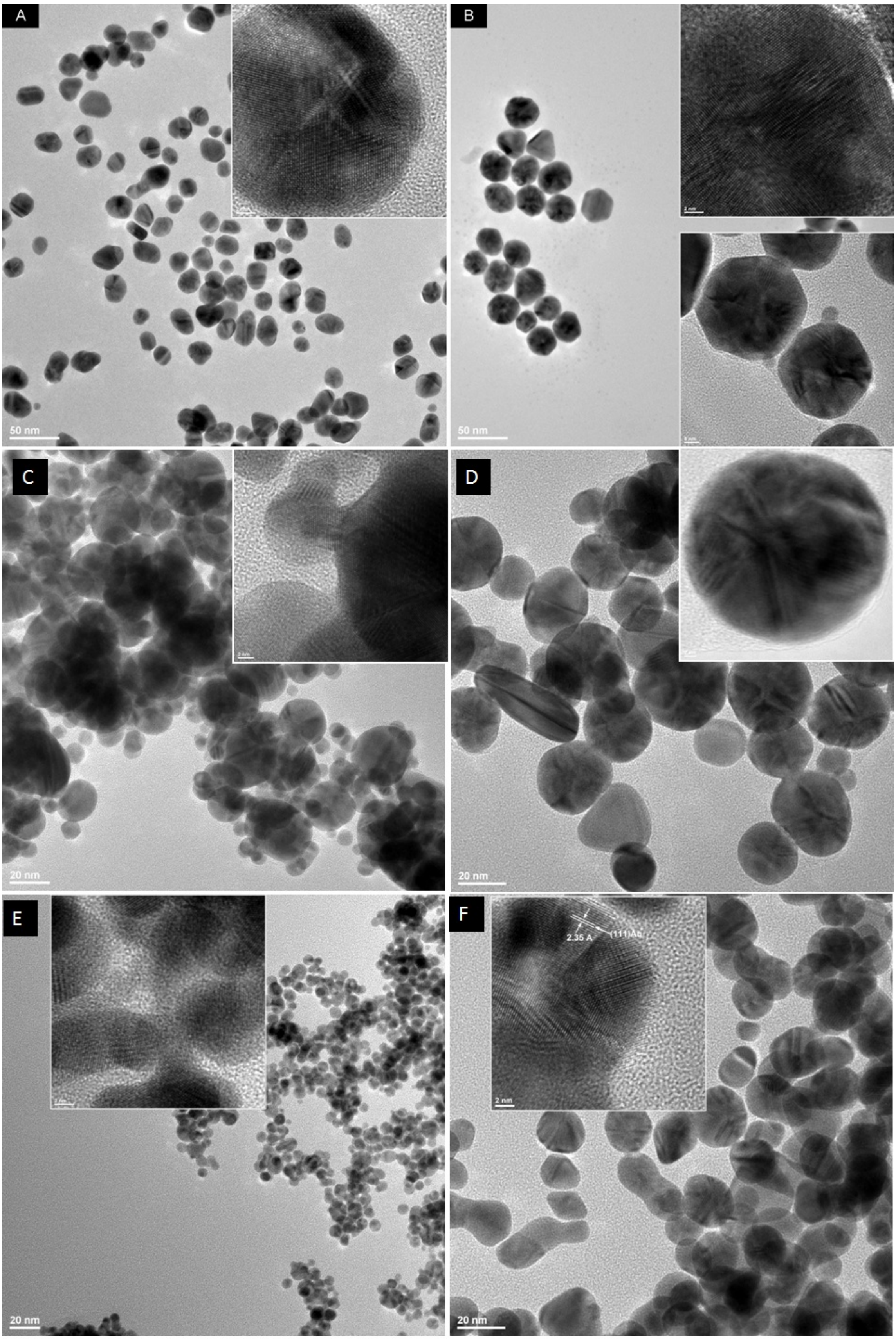


Fig 1. TEM and HR-TEM images presenting the influence of dendrimer concentration and generation over the dimension of the composite nanoparticles: A - dispersed Au-citrate-2.5 *nanoparticles; B - dispersed* Au-citrate-5 *nanoparticles; C - nanocomposites Au - PAMAM-SA-G2-2.5; D - Au-PAMAM-SA-G2-5; E - Au-PAMAM-SA-G4-2.5; F - Au-PAMAM-SA-G4-5. Morphological details are visible in insets.*

This is explained through the fact that the lower generation dendrimers, as schematically depicted in scheme 1, are open structures favouring crystal growth phenomena from the interior of the framework, while maintaining the shape of the template. Au(III) initially preorganized inside the dendrimer molecules that contains 14 tertiary amines efficiently reducing the metal to metallic gold (Au^0). Then, in a system with excess of gold, the growth of the crystalline phase is possible, and due to dendrimer architecture and stoichiometric reasons, the dendrimer is encapsulated into the final nanocomposite (see scheme 1). The mechanism supposed to occur when the nanoparticles are formed was explained in detail in a previous manuscript [26]. Furthermore, in Figure 1 it can be observed that increasing the amount of dendrimer leads to more complex structures, containing different populations of nanoparticles coexisting. While the nanoparticles obtained using citrate are nearly spherical and dispersed those obtained using dendrimers do present an enhanced tendency to form nanostructured aggregates. Furthermore, using higher generation dendrimers seems to ehnhance, at lower concentration of dendrimer, the formation of connexions between particles as shown in figure 1F and the corresponding inset.

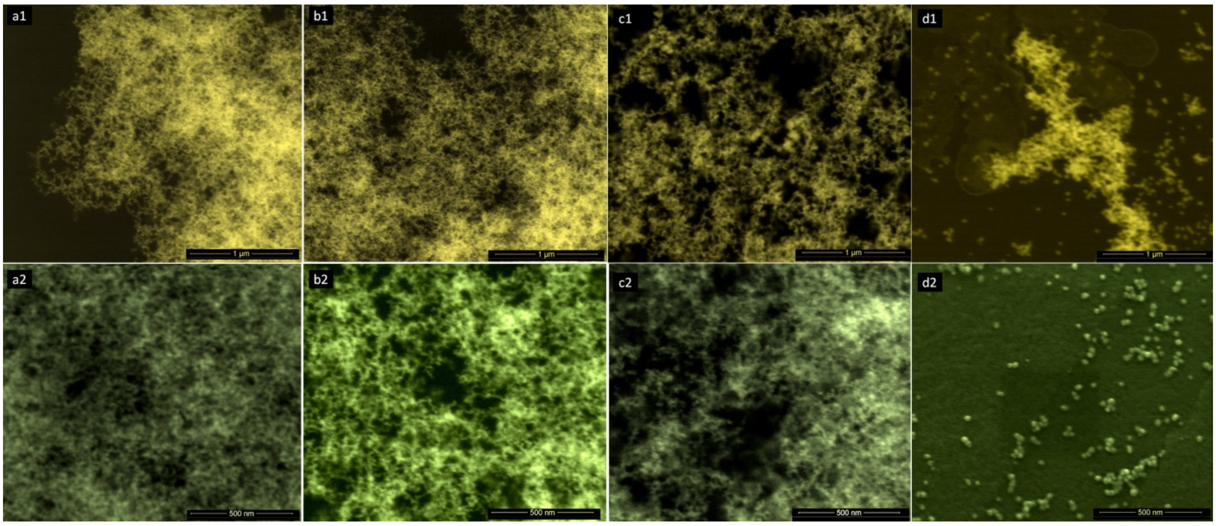


Fig 2. SEM images presenting the different coatings for: a - Au-PAMAM-SA-G2-2.5; b - Au-PAMAM-SA-G4-2.5; c - Au-PAMAM-G3.5-2.5; d - nanoparticles obtained using citrate and used as control (Au(III)/carboxyl 2.5:1). Porous and even nanoporous and nanostructured networks are generated through the self-assembling propensity of the dendrimer-gold composites. a1-d1: images taken at a magnification of 100000x; a2-d2: images taken at a magnification of 200000x. Images have been recoloured for enhanced visibility.

No significant differences in the size of the formed nanoparticles have been noticed for Au-PAMAM-SA-Gi-j and the corresponding Au-PAMAM-Gi-j.

Porous nanostructured layers have been generated with the gold-dendrimer nanocomposites, when coatings of the polymer substrate have been performed (figure 2 a-c). These coatings appear as dense networks with small pores that form through the entanglement of the chains formed by the self-assembled nanoparticles. The nanoparticles obtained using citrate generate also a nanostructured coating, but not porous when compared to the situation when Au-PAMAM-Gi and Au-PAMAM-SA-Gi are used (figure 2d). The self-assembling propensity of the gold-dendrimer nanocomposites is enhanced by the synthesis method since it is widely known that dendrimers do present a high assembling potential.

4. Conclusions

This work presents the formation of crystalline gold-dendrimer nanoparticles efficient as nanostructuring units generating porous and nanostructured coatings. Preliminary effect of the type, generation number and concentration of the dendrimers on the morphology and assembling propensity of the so-formed nanocomposites are presented. Dispersed nanoparticles obtained with sodium citrate have been used as control. Further studies will be devoted to deeper characterization of such nanostructured layers.

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