

Passivated metal superlattices self-assembled around a fullerene onion*

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Recibido el 1 de junio de 2000; aceptado el 17 de julio de 2000

In modern materials science there are two important topics; fullerene research and quantum dot devices. These areas are considered very promising in the nanoelectronics and nanophotonics technology. In the present work it is shown that this two fields can be combined. It is demonstrated that a fullerene onion, which has a Russian doll structure, can act as a nucleation center for an ordered superlattice of passivated metal nanoparticles produced by growth in toluene vapor. Gold metal cores were passivated with dodecanethiol molecules. There were found fullerene onions ringed by gold particles whose first layers tend to mimic the fullerene structure. However as the distance from the carbon core increases the superlattice tends to recover its standard close packed structure, it is shown that the driving force for the self assembly is the interaction between the carbon atoms in the fullerene and the terminal CH₃ groups of the n-alkyl thiol molecules. This appears to be a promising method for the fabrication of metal-coated fullerenes for practical applications.

Keywords: Gold nanoparticles; fullerenes; superlattices and quantum dots

En la ciencia moderna de materiales, dos de los temas de mayor importancia son: la investigación sobre fulerenos y la referencia al desarrollo de dispositivos basados en puntos cuánticos. Estas áreas se han considerado de suma relevancia, con un gran potencial para el desarrollo de la tecnología nanoelectrónica y nanofotónica. En este trabajo se observa que tales campos de la investigación pueden combinarse: se demuestra que una estructura concéntrica de fullereno, puede actuar como un centro de nucleación para la formación de una superred ordenada, de nanopartículas metálicas de oro con moléculas de 1-dodecanotiol. Durante el proceso de crecimiento en vapor de tolueno, las nanopartículas se ordenaron alrededor de la estructura de fullereno, de forma tal que las primeras capas de la superred tienden a mimetizar la estructura de fullereno, de forma tal que las primeras capas de la superred tienden a mimetizar la estructura de este núcleo de carbón. Sin embargo, a medida que se incrementa la distancia con respecto al fullereno, dicha superred tiende a recobrar una estructura estándar de empaquetamiento hexagonal compacto. Se muestra que las interacciones que conducen al autoensamblaje corresponden a la interacción entre los átomos de carbón de la estructura concéntrica y los grupos terminales CH₃ de las moléculas de n-alcilthiol.

Descriptores: Nanopartículas de oro; fulerenos; superredes y puntos cuánticos

PACS: 61.46.+w; 68.65.+g; 61.82.Rx

1. Introduction

The discovery of fullerenes, and the possibility of synthesizing them in macroscopic quantities [1], has produced one of the most important areas in materials science research. The possibility of using carbon nanotubes as electronic devices such as one-dimensional conductors [2] appears to be very promising. The interaction of metals with fullerenes is one of the main research subjects in this area because of the importance they have got for future practical applications. Huo *et al.* [3] have recently shown the synthesis of metal-C₆₀ films. The strong metal-C₆₀ interaction leads to charge transfer from the metal to the C₆₀ at the interface between them.

Another very important advance in nanoelectronic devices is the synthesis of superlattices of passivated metal nanoparticles [4]. Robust structures with different lattice arrays can be formed with gold using n-alkyl thiol molecules as passivating agent. Wetthen and coworkers and other groups [5-7] have shown that superlattices of nanoparticles with either *bcc*, *fcc*, *hcp* or pseudo tetragonal structure can be produced by varying the size of the metal core and the length of the thiol carbon chains. Those superlattices appear as im-

portant candidates for single electron tunneling devices [8]. In the present work we show that gold nanoparticle superlattices can be nucleated around a fullerene structure. In particular we show that the onion cages, reported by Ugarte *et al.* [9], can act as self assembly centers for nanoparticle superlattices.

2. Materials and methods

Gold passivated particles were produced by the method of Brust. *et al.* [4] who used 1-dodecanethiol as passivating agent. A copper electron microscope grid covered with a carbon film containing onion fullerene cages was used as a substrate to produce the superlattice. A solution of passivated gold nanoparticles in toluene was deposited on the grid, and then it was placed in a chamber with toluene vapor. The superlattice was grown at 55°C during 36 hours. The grid was observed by TEM. A JEOL 4000-EX and a JEOL-2010 microscopes were used for the observations. The focus condition was optimized for either high-resolution observation of the atomic columns of gold (Scherzer focus) or to an optimum defocus for the nanoparticle superlattice contrast [10].

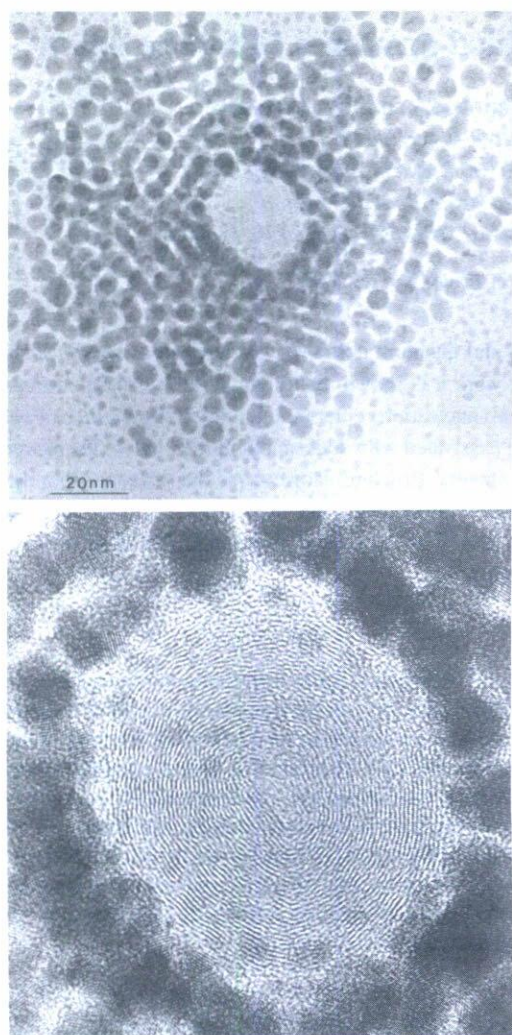


FIGURE 1. TEM Image of a nanoparticle superstructure which is formed around a fullerene onion: a) general view of the structure b) magnified view of the central part of the nanoparticle superlattice showing the fullerene onion structure. Note that the particles in the edge of the fullerene cage mimic the fullerene structure.

3. Results and discussion

A typical resulting structure is shown in Fig. 1a. The passivated metal nanoparticles form an ordered superlattice around a fullerene onion. A magnified image of the central part of the structure is shown in Fig. 1b the metal nanoparticles are not observed on the top of the fullerene cage but only on the sides forming a ring around the fullerene. An idealized model of the composite metal-fullerene is shown in Fig. 2. The fullerene cage in Fig. 1a has 32 layers and has a size 25 nm.

A simple model shows that when the number of layers on the fullerene cage is increased, the external geometry becomes flatter. Therefore a toluene solution of passivated particles is deposited on the surface of the amorphous carbon grid, using toluene vapor to diffuse them until reaching the

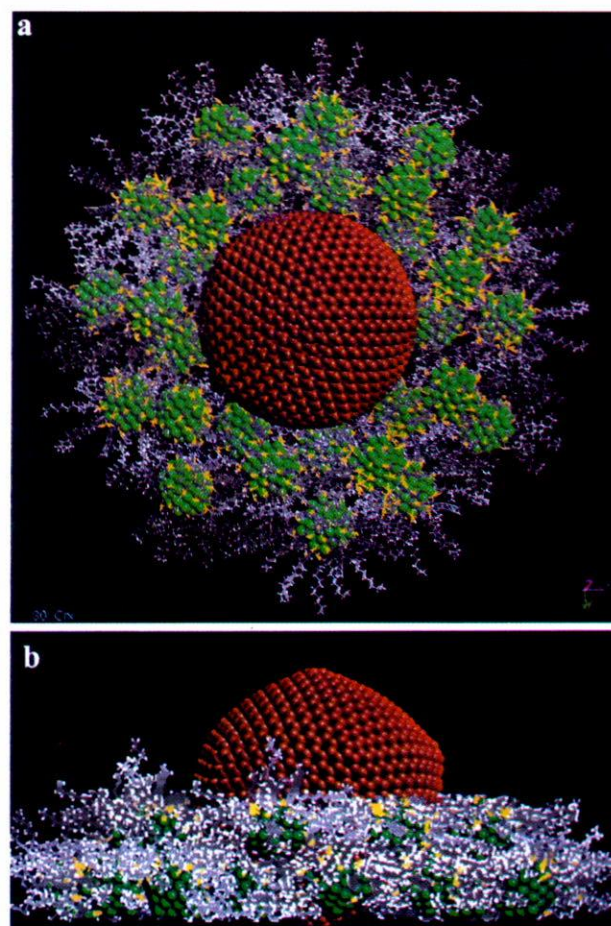


FIGURE 2. Ideal Model of the structure observed in Fig. 1. The gold nanoparticles are shown in green. Dodecanethiol molecules are shown in gray (C), white (H) and yellow (S). The fullerene onion is shown in brown. The structure is shown in top view (a) and side view (b).

fullerene cage. Because of the flat surface a belt is produced around the cage. The fact that no particles are observed on the top of the structure suggests that the thiol-passivated particles have a limited mobility on the cage surface and relatively strong bonds are formed.

The structure of the superlattice tends to mimic the fullerene structure in the first two or three layers. This is demonstrated by the selected area diffraction pattern, which presents a ring structure similar to that produced by the fullerene cages. However as the distance from the center increases the superlattice relaxes and the structure tends to be close packed. A close examination of the high-resolution image of the particles indicates that the belt is formed by two layers located at different heights. The selected area and high dispersion diffraction pattern of the whole superlattice is shown in Figs. 3a, 3b and 3c. The figure indicates an average hexagonal lattice. Under the experimental growth conditions, this would be the expected superlattice structure, if no fullerenes were present [5]. Therefore the metal-fullerene interaction is only of short range.

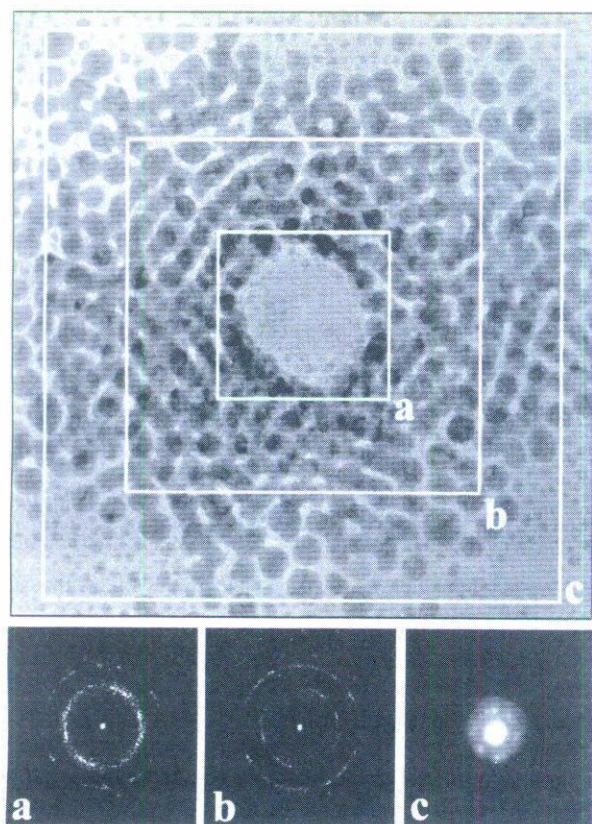


FIGURE 3. Diffraction patterns from a nanostructure superlattice formed around a fullerene cage. The patterns a)-b) correspond to selected area diffraction patterns from the indicated regions c) corresponds to a high dispersion diffraction pattern of the whole superstructure.

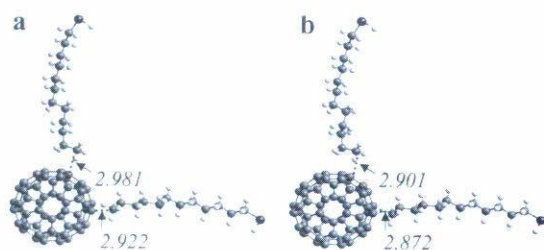


FIGURE 4. Molecular dynamics simulation of the interaction between a fullerene C_{60} -Molecule and a dodecanethiol molecule. Note the twisting produced on the thiol molecule as a result of the interaction between both molecules. a) shows initial stage b) final stage after relaxation. Some of the bond distances are shortened.

In order to understand the results we have made calculations applying the density functional theory [11] using the cerius² quantum mechanics workbench [12]. In particular we used the modules DMol [13] and Mopac [14]. Calculations were performed in a silicon graphics computer with a R10000 processor.

In the model we used 1-dodecanethiol as the passivating agent and a fullerene C_{60} molecule. The resulting structure is shown in Fig. 4, where an interaction between the carbon and

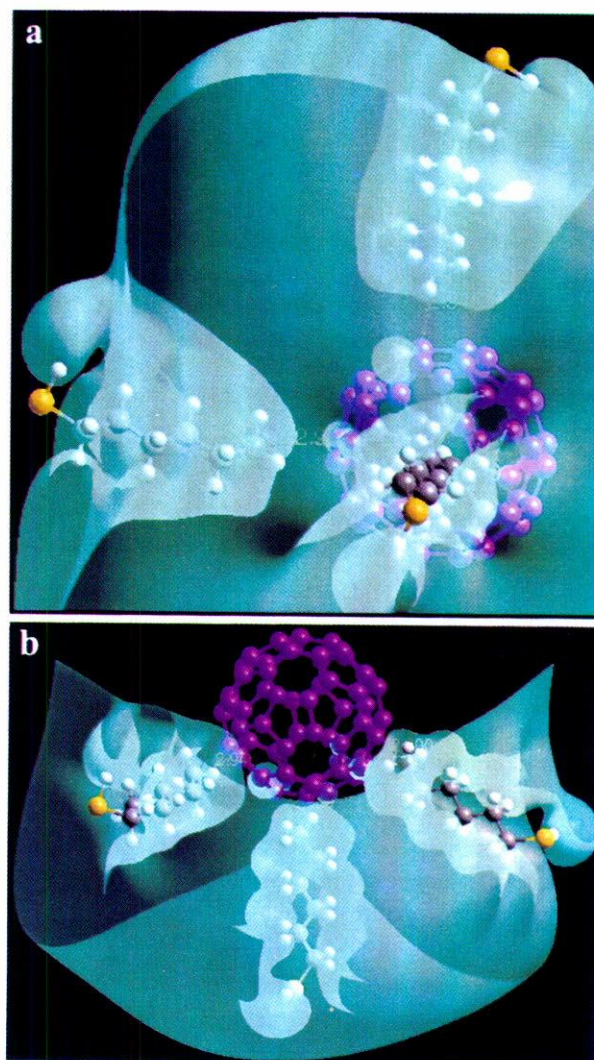


FIGURE 5. Plot of the electrostatic field produced on a system of a C_{60} molecule with five dodecanethiol molecules. The field assumes a symmetrical nearly spherical distribution, which follows the symmetry of fullerene cage. a) and b) shows the top and side views.

the terminal CH_3 group of the thiol molecule is formed. We have also calculated the electrostatic potential for a system formed by a C_{60} molecule and five dodecanethiol molecules. The result is shown in Fig. 5. The iso-potential surfaces follow the fullerene contour and the thiol molecules arrange in the expected fashion. It has been shown that in the formation of superlattices of thiol-passivated particles the main interaction is the one among thiol molecules [15] being the interaction between metal cores only 10% of the interaction force. Therefore the resulting structure near the fullerene cage will be mostly defined by the fullerene-thiol interaction.

We found that there is a strong tendency to form superlattice of nanoparticles around fullerenes structures. In fact in the samples observed there was a superlattice around every fullerene anion. However we also found that nanoparticles can be self-assembled around graphene sheets with the parti-

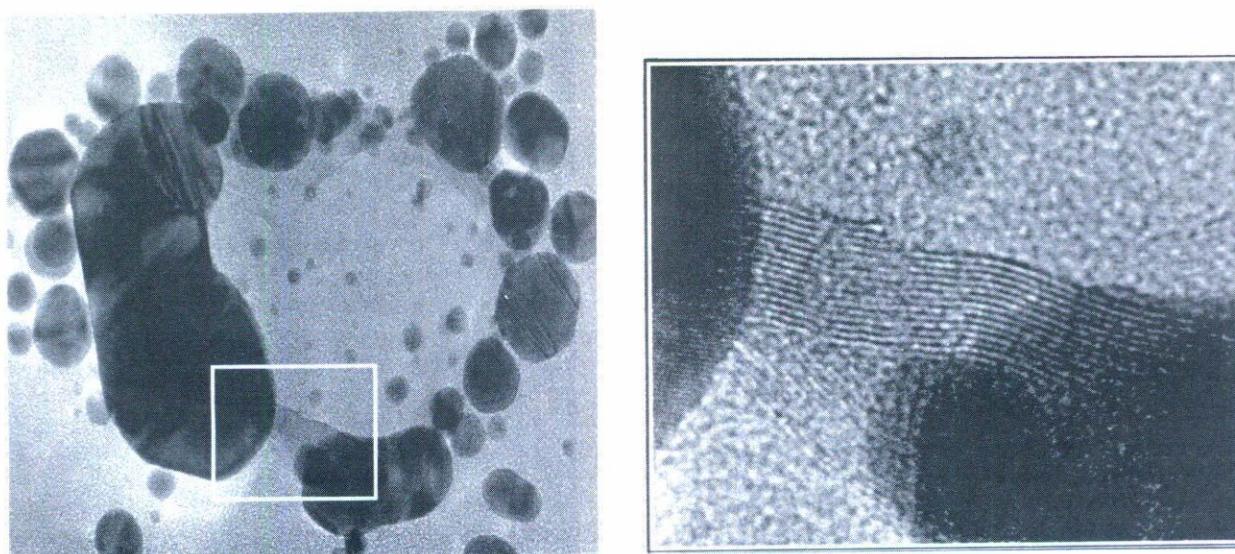


FIGURE 6. Examples of bridges between passivated gold nanoparticles formed around graphite ribbons. The nanoparticles follow the curvature of graphene. A magnified frame is shown in which the graphite bridges are clearly observed.

cles following the curved shape of the graphene, which is presented as a graphite ribbon. In several cases we observed the formation of graphite bridges between particles as shown in Fig. 6.

Our results suggest the possibility of forming metal-coated fullerene structures, which will open up the way for many exciting applications of fullerenes in nanoelectronics.

Acknowledgments

The authors are indebted to CONACYT for financial support through the grant "Coloides Cuánticos, Puntos Cuánticos y Nanoparticulas". We are indebted to Luis Rendon, J. Arenas, A. Camacho, M. Pérez, R. Reglero for technical support and to Maria Eufemia Fernández for helping on the theoretical calculations.

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