

Gold nanoparticles grown on multiwall carbon nanotubes^{*}

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A new method of decorating carbon nanotubes (CNTs) with metal nanoparticles (NPs) is proposed. It consists in evaporating a metal layer on CNT deposited on a substrate and subsequent annealing at 400 °C. It is shown that after annealing the Au layer is reshaped and metal nanoparticles are formed. The size of NPs depends mostly on the initial thickness of the metal layer and the thickness of the nanotubes. The Au layers are not detached when decorated CNTs are redispersed in a solvent and deposited again on a support. Au NPs on CNT can be functionalised by well known methods of thiol adsorption and used e.g., in sensors.

Key words: *gold nanoparticles; carbon nanotubes; reshaping*

1. Introduction

Recently, a renewal of interest in gold nanoparticles (NPs) has been observed since the discovery of their catalytic activity towards low temperature CO oxidation [1]. There is also a considerable interest in the deposition of metal nanoparticles on carbon nanotubes (CNTs) using various methods (see e.g., [2]). In most cases, the NPs were synthesized in solution and attached or covalently bound to CNTs. It was also shown that nanotubes with deposits of Au [3], Pt [4], or Ag [3] NPs can act as low pressure gas sensors. Metal nanoparticles on solid supports, including CNTs, can be obtained by metal evaporation. The size and shape of the NPs formed depend on evaporation conditions and eventually on subsequent annealing. The most studied was deposition of gold [5–7] and silver [8]. For Au, the influence of support temperature and purity was also investigated [9, 10]. It was found that annealing conditions depend on the thickness of the Au layer and on the surface energy of the support. Thin, non-

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continuous layers reshape by coalescence of Au aggregates. This process leads to a decrease of surface energy of the metal but, to be observed in a reasonable time, it requires a sufficiently high temperature, so that the clusters are mobile. Warmack [11] observed coalescence of 2 nm Au films on SiO₂ in the temperature range 200–800 °C. After 4 min at 200 °C some coalescence was already visible, and after the same heating time at 400 °C the effect was pronounced – a twofold increase in the particle size was observed. A thicker, continuous layer was found to reshape at much higher temperatures. Heyraud [12] studied dewetting of thick (300 nm) gold layer on graphite and found that annealing at 1000 °C for 50 h is necessary to obtain an equilibrium shape of Au crystals (few microns in diameter).

In this paper, we present the results of decorating multiwall carbon nanotubes (MWCNT) with gold nanoparticles by vacuum evaporation of continuous layers and subsequent annealing. We discuss the effect of the thickness of the evaporated layer, and the effect of annealing conditions on the size and form of Au NPs.

2. Experimental

Aligned multiwall carbon nanotubes were synthesized by aerosol-assisted catalytic chemical vapour deposition (CCVD) from toluene/ferrocene solution in the laboratory of Dr. M. Mayne-L'Hermite (CEA Saclay, France). CNT come from the synthesis in the form of a carpet, the nanotubes being aligned nearly perpendicularly to the carpet base. The purity of this material is high; it contains only a small amount of by-products [13].

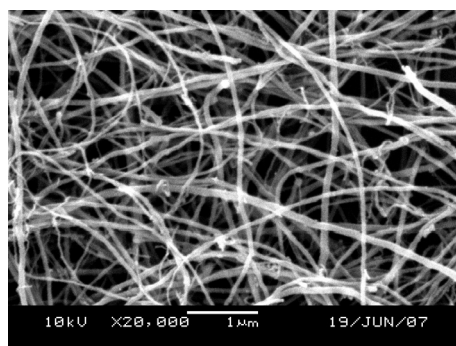
Carbon nanotubes were dispersed in trichloromethane in an ultrasonic bath for 1.5 h. The solution was cast on Si wafer and after the solvent evaporation it was left for half an hour in an oven, heated up to 400 °C to remove residual impurities. At this temperature, the nanotubes are not oxidized, but residues of amorphous carbon or solvent impurities are removed. Then Au was deposited on the surface of the specimen, using Jeol JFC – 1200 Fine Coater. In most experiments, the Au layer was deposited twice from two sides, at an angle of 45°. Such a procedure should assure a more uniform covering of the nanotube surface. However, no significant difference was observed in NPs formation on CNTs oriented parallel or perpendicular to the evaporation direction. The initial Au layer thickness given in the text was determined using atomic force microscopy (Nanoscope IIIa, Veeco Instruments) on a flat support. In the next step, the specimens were annealed at 400 °C in air in a home-made oven, which resulted in reshaping of the Au layer. The samples were investigated using a Jeol JSM – 5500LV scanning electron microscope.

3. Results and discussion

Figure 1 presents a SEM image of CNTs deposited from CHCl₃ solution on Si wafer after evaporation of gold. The thickness of the Au layer on a flat Si surface is

11 nm, and that is much smaller than the average thickness of the nanotubes. These images of the CNTs prior to Au evaporation and after evaporation are very similar, only the contrast is slightly increased. No individual nanoparticles can be seen, which proves that the nanotubes are uniformly covered with gold.

Fig. 1. SEM image MWCNTs dispersed in CHCl_3 and deposited on Si, covered by an 11 nm thick layer of Au



The image of such a sample after annealing at 400 °C is shown in Fig. 2. It can be seen that the gold layer on the nanotubes and on the Si support undergoes reshaping (dewetting) and Au nanoparticles are formed. The size of nanoparticles decorating the nanotubes depends on the thickness of the nanotubes. In the case of thinner nanotubes, the maximum size is limited by the nanotube thickness. On thicker nanotubes one can see bigger and smaller NPs. Few NPs (like those indicated by an arrow in Fig. 2) have oblate shapes and are longer than the CNT thickness. The NPs formed on Si are smaller as compared with these formed on thicker CNTs and their size is more uniform. The difference can be explained by different surface energy of CNTs and Si. Similar effect was observed also comparing reshaping of Au on HOPG with other supports [14].

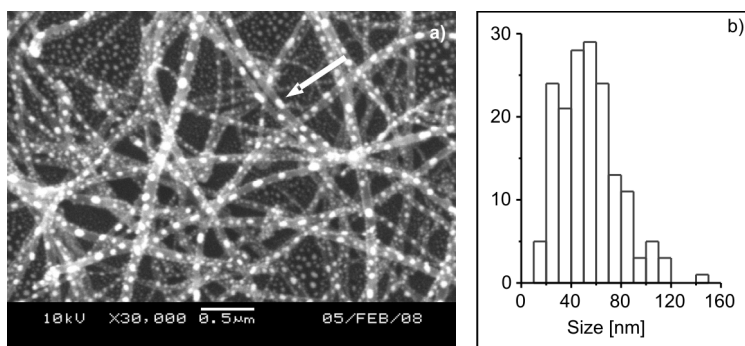


Fig. 2. SEM image of Au nanoparticles (a) formed on MWCNTs and on Si support by annealing a 11 nm gold layer for 10 min at 400 °C (mean size of NPs on CNTs is 55 nm), and the size distribution (b) of the NPs on 4 images of different regions of the same sample. In the case of oblate particles, the longest axis is taken as the NP size

Figure 3 shows an image of the MWCNTs with Au NPs formed by reshaping of an evaporated, 15 nm thick Au layer. It can be seen that, in this case, the nanoparticles

are much bigger (mean size increases from 60 to 130 nm and many of them have oblate shapes). Thus the thickness of the deposited gold layer is a very important factor. Also, the difference in size of the NPs on thinner and thicker CNTs (Fig. 2) can be attributed to the Au layer thickness, because the amount of Au deposited on the curved surface of the CNT is smaller than that on the corresponding flat surface. Thicker Au layers require more time for reshaping.

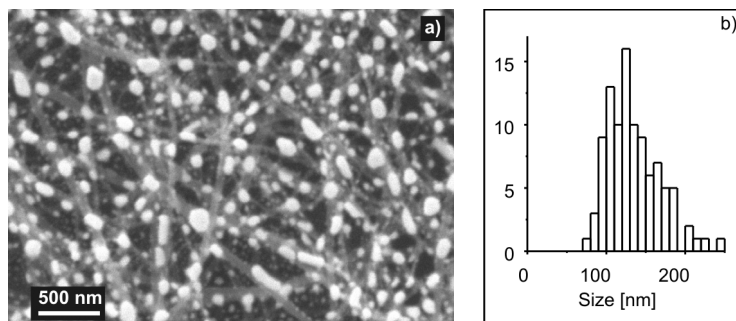


Fig. 3. SEM image of Au nanoparticles (a) formed on MWCNTs by annealing a 15 nm gold layer for 15 min at 400 °C. Mean size of NPs on CNTs is 135 nm and the size distribution (b) of the NPs on 4 images of different regions of the same sample. In the case of oblate particles, the longest axis is taken as the NP size

The size of the nanoparticles can be also controlled to some extent by the annealing time and the temperature but only at the initial stage. After some time the NPs are formed and the effect of longer annealing at the same temperature becomes negligible. The images shown in Figs. 2 and 3 correspond to such an “equilibrium” NPs size after annealing at 400 °C. At higher temperatures the annealing time sufficient to obtain NPs is much shorter, and for instance for a 11 nm Au layer at 600 °C it is only 10 s.

The evaporated layers adhere well to the nanotubes, thus they can be redispersed in solvents and deposited again on a support. A SEM image of such redeposited CNTs is practically the same as that shown in Fig. 1. Such a sample can also be annealed and the image of such a redispersed sample is shown in Fig. 4.

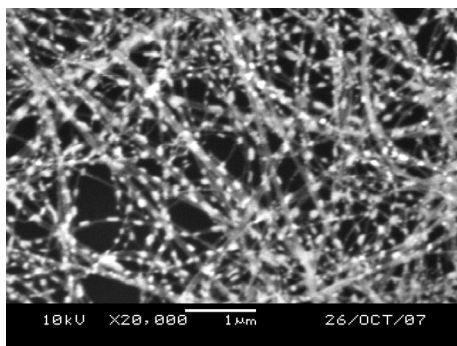


Fig. 4. SEM image of Au nanoparticles formed on MWCNTs after evaporation of Au layer (15 nm), redispersion in CH_2Cl_2 , deposition on Si and annealing for 15 min at 400 °C

It seems that in the case of the layers deposited on CNTs, the process of reshaping is easier than on flat surfaces because the metal is deposited on CNTs in a form of stripes with thin edges on the sides of CNTs. Such structures can more easily separate into smaller particles starting from these thin edges (Fig. 5).

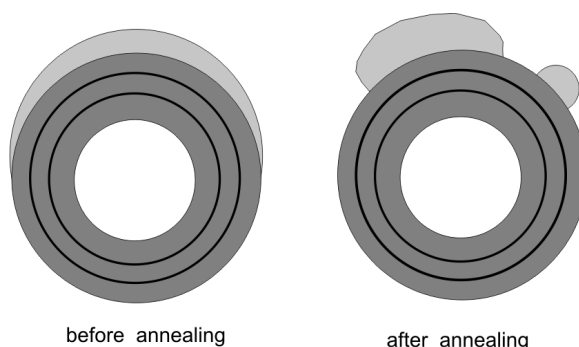


Fig. 5. Schematic representation of Au layer on a MWCNT after evaporation and after reshaping

4. Conclusions

One can obtain CNT decorated with Au nanoparticles by vacuum evaporation of gold and subsequent annealing. The size of the nanoparticles can be controlled by changing the thickness of the deposited gold layer and the annealing conditions. Such gold-decorated carbon nanotubes can be redispersed in a solvent and used e.g., to produce nanocomposites. They can be functionalised by taking advantage of strong thiol adsorption on gold.

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