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Behavior of size selected iron–platinum clusters soft landed on carbon nanotubes

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ABSTRACT

Nano-hybrid systems have been prepared by UHV deposition of size selected iron–platinum clusters on multi-walled carbon nanotubes. Analyses of the resulting morphologies put into evidence the ability of "large" bare clusters (typically few nanometers in diameter) to diffuse on the nanotube surface. A comparison between cluster behaviors on different carbon based surfaces reveals a low cluster-carbon nanotube interaction and a possible effect of the surface curvature on the cluster diffusion process. Moreover, the high selectivity to defects and the specific cluster–cluster interaction leading to a local organization of the FePt clusters on nanotubes open perspectives for various applications.

1. Introduction

Due to the possibility of combining the unique physical and chemical properties of carbon nanotubes (CNT) with original properties of nanoparticles (NPs) in one single structure, nano-hybrids are assumed ideal materials for a wide range of applications (fuel cells, heterogeneous catalysis, hydrogen storage, chemical and biochemical sensing applications...) [1]. Consequently, there is a great deal of interest in attaching nanoparticles to nanotube surfaces. Among inorganic materials, specific efforts have been devoted to magnetic particles for the functionalization of carbon nanotubes. This is related either to their promising applications (nano-probes for magnetic force microscopy (MFM), biosensors, and drug delivery [2–5]) or more fundamentally, for the opportunity provided by such systems for the measurements of intrinsic properties of nanoparticles [6,7].

Up to now, several approaches, mainly chemical [8–16], have been considered to prepare such systems. Depending on the applications or on the fundamental questions investigated, different "model" samples are highly desirable. More specifically, a control of size selected isolated nanoparticle position appears extremely promising in order to study the intrinsic properties (magnetic for instance) of such particles or for applications in MFM. Conversely, dense assemblies of size selected particles, ideally self-organized, are required for applications in the domain of catalysis for example. To develop and optimize these specific samples (isolated localized NPs or NP dense assemblies) a better understanding of both nanoparticle–surface (size effect, CNT curvature effect...) and nanoparticle–nanoparticle interactions and their incidence on nucleation and growth processes appears inescapable. In this domain some experimental and theoretical studies have been devoted to analyze and quantify the diffusion and the interaction of single atoms on CNT [17–22], but to our knowledge, naked cluster diffusion and their interaction with carbon nanotubes have been poorly studied theoretically [23,24] and remained unexplored experimentally.

With this goal, we propose an original physical approach consisting of a UHV direct deposition of preformed size selected bimetallic nanoparticles on as prepared (i.e. without specific functionalization) carbon nanotubes. Since the clusters synthesis is ligand free and since clusters are deposited in UHV conditions, this approach is extremely well suited to characterize properly the interaction between naked clusters and nanotubes. In this paper, from a comparison between the cluster behaviors on different carbon based surfaces, we will put into evidence for the first time the ability of bare nanometers clusters to diffuse on CNT surfaces. This diffusion associated to a high selectivity of clusters to defect can then be exploited in view to elaborate samples for specific applications.

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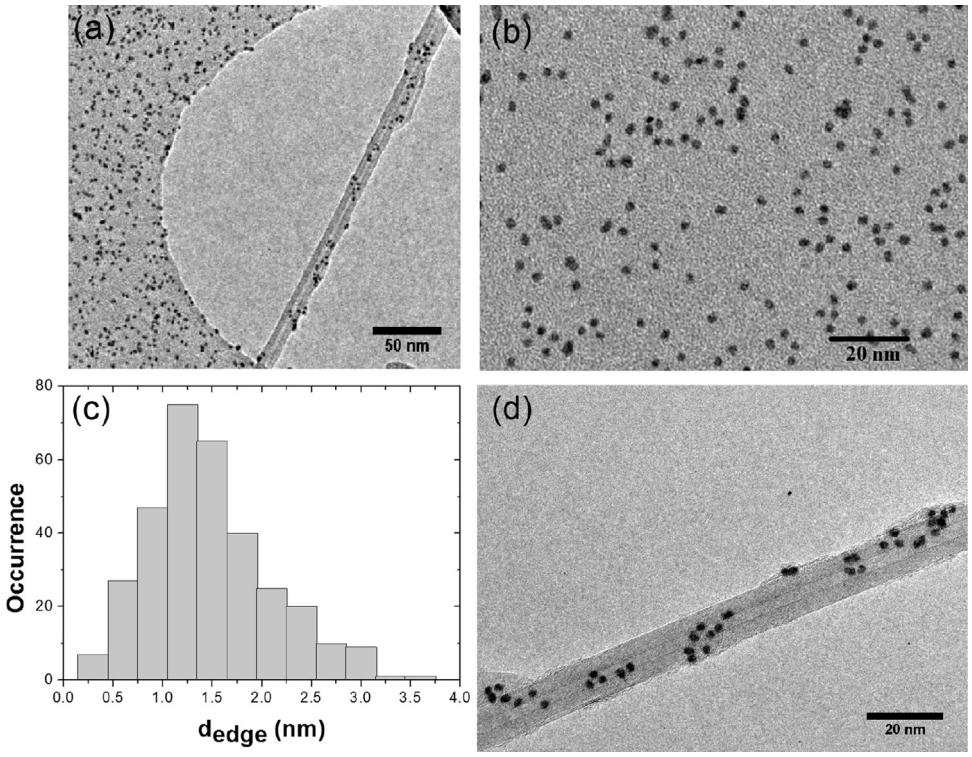

Fig. 1. TEM images of typical morphologies obtained after deposition of 2.2 nm FePt clusters. (a) On CNT and amorphous carbon. (b) On amorphous carbon. (c) Distribution of the distance between first neighbor cluster edges (d_{edge}) on CNT. (d) On CNT.

2. Experimental

Size-selected bimetallic FePt clusters have been synthesized using a laser vaporization source [25,26] and deposited on multiwalled carbon nanotubes (MWNT), highly oriented pyrolitic graphite (HOPG) and amorphous carbon layer under UHV conditions. Briefly, a plasma created by the impact of a Nd:YAG (yttrium aluminum garnet) laser beam focused on a metallic rod is thermalized by injection of a continuous flow of helium at low pressure (typically 30 mbar) inducing cluster growth. Clusters are subsequently stabilized and cooled down in a supersonic expansion while charged clusters are size selected with an electrostatic deviator [27]. With this size selection, the mean cluster size is adjustable with the voltage applied on the deviator and the relative cluster size dispersion becomes lower than 10%. Moreover, the low kinetic energy of clusters (typically 0.1 eV/atom) gained during supersonic expansion ensures the absence of fragmentation upon impact on the substrate [28]. In the case of bimetallic clusters, the composition of the cluster corresponds to the initial rod one [29]. Before cluster deposition, CNT are dispersed in solution and collected to holey carbon grids. The incident cluster flux is measured by a pico-amperemeter and samples are observed by TEM (Topcon 002B microscope operating at 120 kV) after transfer to air without any incidence on the final morphologies [30]. The cluster flux and the time of deposition are fixed to 2.2×10^8 clusters cm^{-2} s^{-1} and 30 min respectively, ensuring a constant surface coverage of about 2% for all experiments. A mean diameter of 2.2 nm has been chosen for the incident clusters.

In this work, multiwalled carbon nanotubes of mean outer diameter about 12 nm have been synthesized using a standard electric arc discharge reactor [31]. This technique provides the advantage of growing high crystallinity MWNT without any catalytic particles, very few defects [32] and without amorphous carbon coverage.

3. Results and discussion

FePt clusters are soft landed on a substrate composed by both suspended CNT and amorphous carbon layers. This allows a direct comparison between morphologies obtained on the two surfaces. As shown in Fig. 1(a), drastic differences are observed: while on amorphous carbon the deposited clusters remain isolated and randomly distributed on the surface, on CNT, the aggregation of clusters in islands is clearly observed. Since in both cases, NPs are randomly deposited on the surface, such island formations put into evidence, undoubtedly, their diffusion on the CNT surface.

Oppositely, on amorphous carbon (Fig. 1(b)), as already seen previously for others NPs [33], the high density of defects on the surface is efficient to trap the cluster directly upon impact leading to a high density of isolated particles. While in the case of amorphous carbon, where clusters remain isolated for the surface coverage used here, one can understand easily the size conservation of the clusters from the free to the supported state, it is less intuitive for the CNT surfaces. In this case, as revealed in Fig. 1(c and d), the cluster size conservation (absence of cluster coalescence) is obviously related to the absence of contact between particles composing the islands. According to the structural similarities between CNT and graphite surfaces and to the extensive studies already done on this surface for other clusters, samples of the same particles deposited on graphite have been produced in order to get more insight of these peculiar morphologies. Fig. 2 reveals that, on graphite FePt clusters diffuse and aggregate into large islands. Additionally, islands are composed by non-contacting nanoparticles with incident size conservation (Fig. 2(c)). Moreover, as shown in Fig. 2d, a local spontaneous hexagonal order is clearly seen on the radial distribution function (the radial distribution function, in two dimensions, is $g(r) = P(r)/(2\pi r)$, where $P(r)dr$ is the probability of finding a particle at a distance d from another particle in the interval $[r, r+dr]$), with a characteristic distance of 1.2 nm between