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## Self-organisation of size-selected $\text{Co}_x\text{Pt}_{1-x}$ clusters on graphite.

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

[www.rsc.org/](http://www.rsc.org/)

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Sub-monolayer thin films morphologies obtained by deposition of size-selected  $\text{Co}_x\text{Pt}_{1-x}$  clusters on graphite have been analyzed for different values of  $x$ . In all cases, the preformed clusters can easily diffuse on the surface and gather to form islands of clusters. By changing the cluster stoichiometry, very different morphologies can be obtained, going from large ramified islands to “bunches” of non-contacting incident clusters. We put into evidence that the introduction of platinum atoms in the incident particles drastically changes the interaction between clusters and offers the opportunity to control the coalescence process between them. In this way, by modifying the cluster reactivity, a local self-organization of size-selected magnetic nanoparticles can be achieved.

## ARTICLE

**A. Introduction**

Due to their extremely small size and large specific surface area, nanoparticles possess original physical and chemical properties quite different from those of larger particles of the same materials. Thus, they are expected to have many potential applications as optoelectronic, semiconducting, or magnetic materials, as well as in catalysis<sup>1,2,3,4</sup>. Additionally, arrays of monodisperse nanoparticles would allow one to address single clusters properties (same environment for each particle), or to obtain interference phenomena (i.e. large amplitude responses). As a consequence, growing arrays of identical nanostructures on a surface is of great interest both for applied and fundamental physics. In that view, the use of spontaneously pre-patterned substrates at the nanometer scale has revealed to be a promising way to induce the nucleation and growth of clusters on specific sites. In the case of magnetic particles, physical approaches based on atomic deposition have not only led to regular networks of clusters, but also to narrow size distributions with well-defined properties. Growth of Co clusters on the Au (111) reconstructions<sup>5</sup> and on vicinal gold surfaces [Au (788) and Au (677) for instance<sup>6</sup>] are some of the most famous examples with large unit cells ( $15 \times 7 \text{ nm}^2$ ,  $3.9 \times 7 \text{ nm}^2$  and  $3.4 \times 8.1 \text{ nm}^2$  respectively). However, it still remains necessary to improve the magnetic stability of such small nanostructures against thermal excitations by increasing for instance the magnetic anisotropy energy (MAE)<sup>7</sup>. For that purpose, mixed clusters like  $\text{Co}_x\text{Pt}_{1-x}$  seem to be good candidates especially in the  $L1_0$  or  $L1_2$  phase<sup>8</sup>. Unfortunately, due to different behaviors of each atomic species on the surface, the formation of mixed cluster arrays still remains a challenge by atomic deposition not only in term of organization but also in term of stoichiometry<sup>9</sup>.

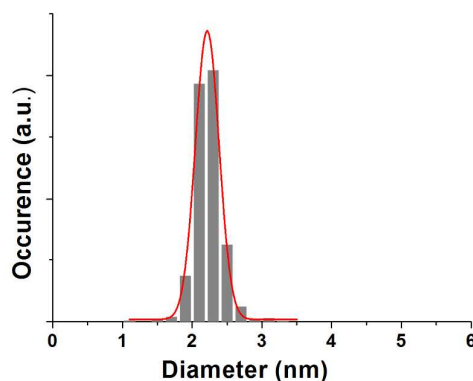
The low energy cluster beam deposition (LECBD)<sup>10</sup> of size-selected CoPt clusters appears as an original approach to circumvent these difficulties. Indeed, this technique allows ultrahigh vacuum (UHV) deposition of preformed clusters in gas phase without fragmentation at their arrival on any substrate. In this case, the surface coverage can be fully controlled (without changing the particle size) and the 3D shape of the supported particles allows larger sizes than 2D “pancakes” obtained by atomic growths<sup>5,6</sup>. Moreover, since the laser vaporization process preserve the stoichiometry of the target, alloyed particles of well-defined composition can be directly obtained by using mixed rods<sup>11</sup>. In addition, besides the fact that one can change the composition of the incident cluster, another benefit of using clusters lies in the possibility to include a small amount of impurities into that species to build a large variety of new architectures<sup>12,13</sup>. In this domain, we have recently reported original results of spontaneous organization for size-selected preformed platinum and  $\text{Au}_x\text{Pt}_{1-x}$  clusters deposited on graphite under UHV<sup>14,15</sup>. More specifically, we have put into evidence that the presence of platinum atoms in size selected gold clusters, can strongly modify their behavior on graphite surfaces. In particular, it leads to thin cluster films with a morphology completely different from the usual gold ramified islands composed of connected particles<sup>15</sup>. These changes in morphology, i.e. cluster size conservation and spontaneous local organization, have been attributed to an enhancement of the reactivity of bimetallic clusters (the surface origin of this behavior is made clear from the effect of a deposition pressure change<sup>23</sup>). By playing on the kinetics of cluster surface passivation, we have put into evidence that with a well-chosen set of experimental parameters, it becomes possible to spontaneously organize  $\text{Au}_x\text{Pt}_{1-x}$  bimetallic nanoparticles<sup>15</sup> with different value of  $x$ .

In this paper, we analyse the possibility to extend this approach to magnetic mixed  $\text{Co}_x\text{Pt}_{1-x}$  clusters. With this goal, we will first present the morphologies obtained with pure clusters. Then, the effect of incorporation of platinum atoms in cobalt clusters on the spontaneous organization will be discussed. The potentiality of this approach to locally organize mixed clusters on graphite is finally put into evidence in the case of FePt clusters.

**B. Experimental**

Size-selected bimetallic  $\text{Co}_x\text{Pt}_{1-x}$  clusters have been synthesized using a laser vaporization source and deposited on Highly Oriented Pyrolytic Graphite (HOPG) under UHV conditions<sup>10</sup>. 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 taking place at the exit nozzle of the source. In this study, a quadrupolar electrostatic deflector device, fully described elsewhere<sup>16</sup>, acting as a mass filter of charged incident clusters has been used in order to lower the spread of the cluster size distribution. 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%. Cluster size distributions are characterized by time-of-flight mass spectrometry and by Transmission Electron Microscopy (TEM) after deposition on amorphous carbon grids (Fig. 1)<sup>17</sup>. Moreover, the low kinetic energy of the clusters (typically 0.1 eV/atom) ensures the absence of fragmentation upon impact on the substrate<sup>18</sup>. Particularly interesting for our study, previous RBS and EDX analysis have put into evidence the conservation of the rod stoichiometry in the clusters (with only a few percent deviation from the nominal composition), thus by changing the composition of the rod, one can adjust the composition of the synthesized bimetallic clusters<sup>19,20</sup>. Thus, to study the effect of the incorporation of Pt atoms in the clusters, five metallic rods of  $\text{Co}_x\text{Pt}_{1-x}$  with compositions:  $x = 0; 0.25; 0.5; 0.75$  and 1 have been used in the present work. Moreover, to allow a direct comparison between morphologies and to ensure that changes are only related to concentration effects, all experiments have been carried out at room temperature using almost the same cluster size, incoming cluster flux, deposition base pressure ( $2 \times 10^{-10}$  Torr) and surface coverage. The incident size-selected cluster flux is checked by a pico-amperemeter to be  $2.2 \times 10^8$  clusters. $\text{cm}^{-2}.\text{s}^{-1}$  while a mean diameter ( $D_m$ ) of about 2 nm has been chosen for the incident clusters. The deposition time has been fixed to 30 min ensuring a constant surface coverage of 1.4% for all experiments. According to the random nature of the deposition process<sup>21</sup>, this low surface coverage has been chosen in order to minimize direct formations of  $n$ -mers (*i.e.* particles resulting from contact with or without coalescence of  $n$  incident clusters). Ex-situ TEM observations of supported clusters on graphite are achievable by gluing a copper grid on the HOPG substrate and then lifting it off before observation<sup>22</sup>. We emphasize that lift off processes and transfer to air do not have any impact on the final morphologies as demonstrated previously by in situ UHV scanning tunneling microscopy (STM) observations for pure Platinum clusters<sup>23</sup>.

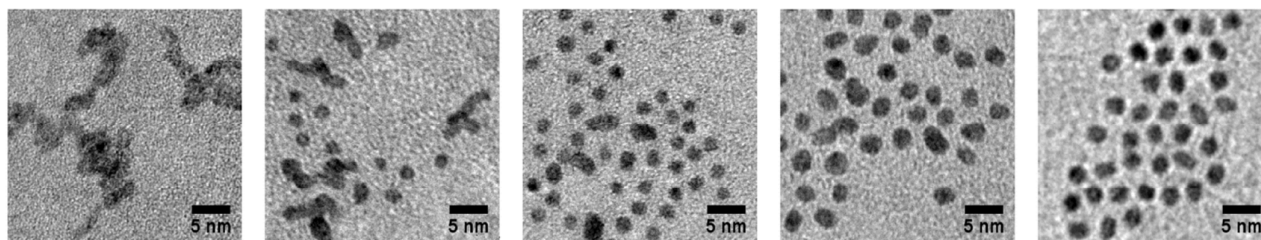


**Fig. 1:** Characteristic size distribution of the incident clusters with a mean diameter  $D_m=2.2$  nm and a relative standard deviation of 8% (case of pure platinum clusters). Note that this size distribution is almost the same for all  $\text{Co}_x\text{Pt}_{1-x}$  clusters and has been obtained by analysis of TEM images of  $\text{Co}_x\text{Pt}_{1-x}$  clusters deposited on amorphous carbon grids:  $D_m=2.2$  nm (for  $x=0$  and  $x=0.25$ ) while  $D_m=1.9$  nm (for  $x=0.5, 0.75$  and 1).

### C. Results and discussion

Figure 2 reveals the dependence of the thin films morphologies on the  $\text{Co}_x\text{Pt}_{1-x}$  cluster concentrations from pure cobalt clusters, ( $x=1$  on the left) to pure platinum clusters ( $x=0$  on the right). In the case of pure cobalt clusters ( $x=1$ ) (Fig. 2, left), ramified islands resulting from an aggregation of incident clusters are formed on the surface. Such morphologies are comparable to the ones previously obtained and extensively studied for gold, silver or antimony clusters for instance.<sup>24,14,25,26</sup> In this domain, it is now well-established that the large diffusion and the aggregation of clusters on a graphite surface generally lead to thin films composed of ramified structures formed by the juxtaposition of nanoparticles in contact with each other. Such morphologies are usually remarkably well-described by Monte Carlo simulations<sup>27</sup>. Comparison between experimental results and theoretical predictions has provided a precise description of nanocluster behavior on graphite surface<sup>24,28</sup>. Briefly, as a general rule, when an incident

cluster arrives on graphite, it can either meet another cluster and forms a new island (nucleation event) or be captured by an already existing island (growth process). During this growth process, an incident cluster sticks to the island irreversibly, without further diffusion along the island edges, so that ramified structures are obtained, the width of the ramifications being related to the magnitude of coalescence taking place when clusters come into contact. Moreover, it has been established that the density of island formed on the surface depends on the incident cluster flux and on the cluster diffusion coefficient, Thus by choosing the incident cluster flux, the deposition temperature (*i.e.* diffusion coefficient) and the surface coverage, one can completely control the island density and the lateral extension of these islands.

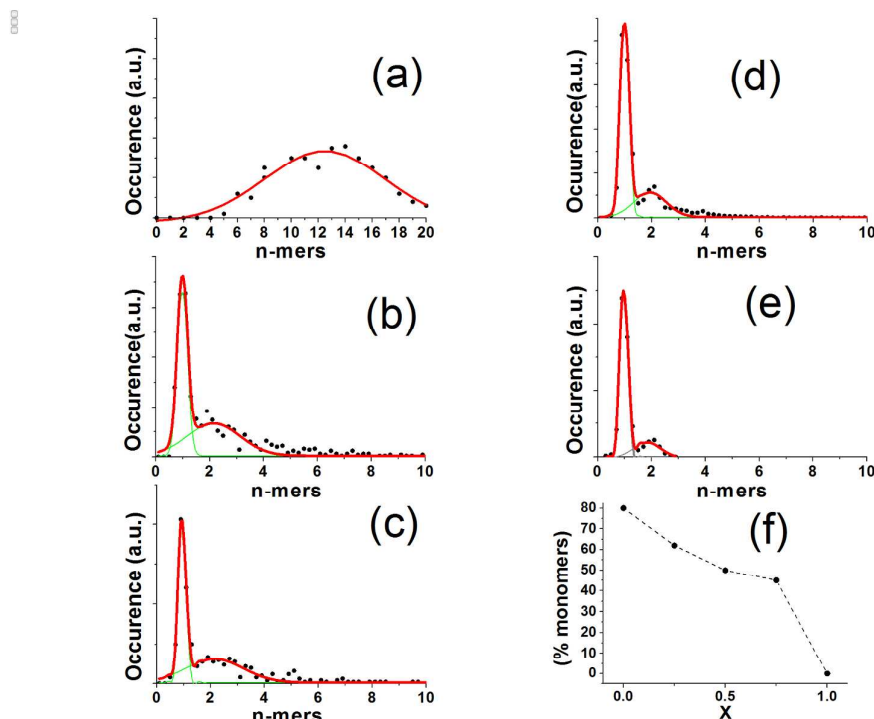


**Fig. 2:** Typical TEM morphologies of  $\text{Co}_x\text{Pt}_{1-x}$  cluster films on HOPG for  $x=1$ ,  $x=0.75$ ,  $x=0.5$ ,  $x=0.25$  and  $x=0$  from left to right.

One can see on figure 2 that films are composed by islands of clusters for all  $x$  values. This put into evidence the ability of clusters to diffuse on such a planar surface for all concentrations. However, there is a gradual evolution of the island morphologies ranging from “conventional” islands composed of connected particles to bunches of isolated particles while decreasing the value of  $x$ . More specifically, by looking, for instance, to a typical individual island of pure Pt clusters (Fig. 2, right), one can observe that it is composed by an aggregation of 2.2 nm incident clusters without contact. A local spontaneous order between nanoparticles can also be detected with a characteristic distance between cluster edges of typically 1 nm. At first, these morphologies appear similar to those previously reported in the case of silver clusters deposited on HOPG, where a fragmentation of fractal islands grown by nanoparticle agglomerations has been activated by thermal annealing or by using a surfactant, as oxide molecules<sup>12,29</sup>. For the thermal fragmentation, primary fragments of coarsened fractal branches exhibit smoothed shapes, whereas in the chemically induced relaxation, evidence of pearled shapes of fractal branches is made. However, such fragmentation processes can be excluded here (where no annealing is performed): according to this mechanism, the diameter of the resulting isolated clusters would not be the one of the incident clusters, the inter-particle distance would not be compatible with the first neighbour distance observed in our samples and the existence of a hexagonal order would not be explained. Additionally, we emphasize that unlike the work of Lando *et al.*<sup>29</sup>, where the clusters are intentionally oxidized in the gas phase, here cluster oxidation has never been detected by time of flight mass spectrometry. Thus, if oxidation occurs, it is only after the nucleation and growth processes on the substrate. To ensure that the island morphologies are not due to a post-relaxation of the fractal island during transfer through air, *in situ* UHV STM observations have been carried out and moreover some samples have been capped *in situ* by an amorphous carbon layer before TEM observation, in order to prevent any oxidation process. In both cases similar morphologies have been observed, excluding a possible effect of *ex situ* oxidation.

According to the well-known extreme reactivity of platinum surfaces to carbon monoxide,<sup>30</sup> CO molecule adsorptions on platinum cluster leading to a modification of the cluster-cluster interaction appears to be the most likely effect to explain our results. As a matter of fact, a simple steric repulsion between clusters with adsorbed CO molecules facing each other with additional short range interaction (due to a charge transfer between oxygen and platinum atoms) can explain the characteristic distance between clusters edges observed here<sup>23</sup>. Note that, this CO adsorption effect on cluster-cluster interaction, is supported by recent observations on platinum nanoparticles deposited on amorphous carbon, where the use of a carbon monoxide saturated electrolyte (as opposed to a oxygen or argon saturated electrolyte) prevent particle agglomeration and coalescence<sup>31</sup>. We emphasize that, even if in our experiment CO is only present has residual molecules in the UHV chamber (no specific introduction

of CO has been done), Longwitz *et al.* have shown that the adsorption of CO is not limited by a pressure offset and can take place for CO partial pressure lower than  $10^{-9}$  Torr<sup>32</sup>.



**Fig. 3:** Size histograms of the particles forming island (note that their size have been normalized to the incident cluster diameter) (a):  $x=1$ ; (b):  $x=0.25$ ; (c):  $x=0.5$ ; (d):  $x=0.75$  and (e):  $x=0$ . (f) Evolution of monomers proportion with the cobalt concentration  $x$ .

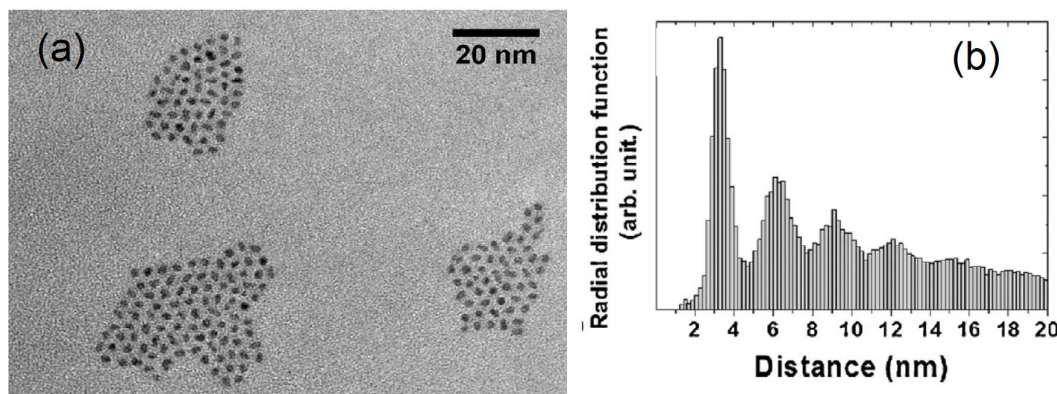
Let us now examine the evolution of particle size distributions with the cluster stoichiometry (see Figure 3). While in the case of pure cobalt clusters ( $x=1$ ) the incident size is completely lost (the mean size corresponds to  $n$ -mers with  $n$  around 12), when increasing the amount of platinum in the incident clusters, the situation evolves towards an absence of contact between particles composing the island and consequently towards a higher monomer proportion (see Fig. 3f, where a proportion of monomers around 80% is reached for  $x=0$ ). Besides, we have also observed that for all values of  $x$  the island density is similar (typically  $2 \times 10^9$  islands. $\text{cm}^{-2}$ ). Since the flux and the deposition temperature are the same for all samples, this puts into evidence that changing the composition of clusters drastically affects their reactivity and thus the cluster-cluster interaction, but does not significantly change the cluster diffusion on the surface (*i.e.* the cluster-surface interaction). Note also that the characteristic distance between particles' edges remains the same (typically 1 nm) whatever the value of  $x$ . This suggests that the final island morphologies are mainly related to the possibility of CO to adsorb on the cluster surface, which depends on the presence of Pt atoms. The evolution of  $n$ -mers proportions with  $x$  is then related to the size of the clusters and must also depend on their atomic structure. Concerning this question, let us note that previous HRTEM studies on thin films of  $\text{Co}_x\text{Pt}_{1-x}$  clusters (2 nm diameter), produced by LECBD and capped with carbon before transfer in air, have revealed truncated octahedron shapes with a chemically disordered face-centered cubic (fcc) phase following a Vegard-like trend for the lattice parameter<sup>20</sup>. Moreover nontrivial redox behaviors have been observed on unprotected clusters films with a rapid and extended de-alloying of CoPt in response to the surrounding gas atmosphere.<sup>33</sup> This illustrates the importance of the surface atoms in these nanoparticles (for 2 nm cluster almost half of the atoms are located on the surface).

Finally in such a system, one could adjust: i) the density of the supported islands by playing with the deposition temperature and the incident cluster flux; ii) the lateral extension of these islands by changing the surface coverage; and finally iii) the “internal” morphology of these islands by modifying the cluster reactivity. For this last point, different parameters are available: the deposition pressure (CO residual pressure), as already demonstrated previously for  $\text{Au}_x\text{Pt}_{1-x}$  clusters<sup>15,23</sup>, the incident cluster size<sup>23,34</sup>, and the amount of platinum in the clusters, as in the present case. Here we have indeed shown that a small amount of Pt



atoms in the incident  $\text{Co}_x\text{Pt}_{1-x}$  clusters can cause drastic changes in the final island morphologies, from large ramified islands to bunches of non-contacting clusters having the size of the initially deposited particles.

To confirm that Pt is very efficient for CO adsorption, what then facilitates a spontaneous organization of clusters on the HOPG surface, we have studied FePt clusters deposited in the same conditions. As presented in figure 4, a nearly complete absence of dimers has been obtained, together with a very nice organization (local hexagonal order, up to a distance larger than 10 nm which is comparable to the island radius). Once more, we can measure a well-defined distance of 1.2 nm between non contacting cluster edges, which is consistent with the O-O separation of two adsorbed CO molecules facing each other.



**Fig.4:** (a): Typical morphologies observed by TEM obtained by deposition of size selected FePt clusters ( $d_{\text{mean}}=2.2$  nm) on graphite at room temperature; (b): corresponding radial distribution function.

## Conclusions

We have studied thin films (sub-monolayer) of bimetallic  $\text{Co}_x\text{Pt}_{1-x}$  nanoparticles, size-selected and deposited on graphite, for different compositions. While in each case the preformed clusters diffuse on the surface and form islands, changing the chemical composition leads to distinct morphologies, going from large ramified islands to “bunches” of non-contacting clusters. Increasing the platinum proportion in the incident particles offers the possibility to avoid contact and coalescence between neighboring clusters. This has been attributed to a change of the clusters reactivity (CO adsorption), which in the end translates as a modification of the cluster-cluster interaction (short range repulsion). Thus, in addition to the usual parameters (particle flux and temperature, which determine the density of islands), changing the clusters stoichiometry offers the extra opportunity to modify the inner structure of cluster islands. We emphasize that avoiding particle coalescence allows us to keep the individuality of the incident size-selected clusters, while surface diffusion remains possible: these are the key ingredients for self-organization. Taking advantage of this behavior, mass-selected low energy cluster beam deposition (MS-LECBD) appears as a promising route for the realization of ultra-high density arrays of magnetic nanoparticles (where the introduction of Pt atoms is also a mean to tailor the magnetic anisotropy)<sup>35</sup>. As a perspective, it would be interesting to take advantage of the absence of contact between neighboring particles to drive a high-quality organization of clusters (better than the Poissonian limit) by deposition on template substrates with a regular array of “nucleation sites” (moiré of graphene grown by epitaxy on metal, vicinal surfaces, etc.).

## Notes and references

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