Surface Science Perspectives

The growth of metal nanoparticles on oxides

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In the past two decades surface science has progressed from research focussed predominantly on the nature of single crystal metal surfaces, to the study of oxides and other inorganic compounds, and more recently to more complex materials such as anchored nanoparticles. The growth, properties and reactivity of very small particles is an area of considerable research expansion for surface science [1], and will continue to be so.

Regarding the nature of nanoparticles, there is considerable interest and debate. Not least of these is the nature of the growth process. As recently highlighted by Campbell [2], the properties of ultra-nanoparticles (which we might define as those in the 1–10 nm size range) can be very different from our preconceptions and from our learning. Thus, for example, small particles appear to be much less stable than might be imagined from the considerations of basic thermodynamics and the Gibbs Thompson equation [2].

A recent paper addresses the growth of nanoparticles on surfaces and shows some surprising features of particle formation: Fujikawa et al. have used STM to try to gain more insight into the growth process of Ni nanoparticles on $TiO_2(110)$ [3]. Previously it had been established that defects of various kinds can be powerful anchor points for nanoparticles. They tend to preferentially nucleate at steps [4] or at surface defects [5]. Hence Fujikawa et al. have purposefully tried to minimise these defects by using a $TiO_2(110)$ surface with a low step density (approximately 70 nm spacing), and by using a relatively high flux rate of Ni from the gas phase (which increases the average coverage of atoms on the surface during deposition and hence the chance of nucleation). As a result they have shown that particles nucleate more or less homogeneously over the terrace, with little evidence of enhancement at the steps. They have found that the morphology of the (110) surface dictates, to some degree, the morphology of the particles (that is, they are elongated in the [001] direction, which is the direction of the channels in the oxide surface). This has also been seen in our own group, and indeed, very long, narrow particles, with a very high aspect ratio of ten can be formed in this way [6], essentially very short nanowires. Fujikawa et al. note that clusters are formed very early on in the deposition process, with a relatively wide spacing between them, confirming that atoms of metal can diffuse over long distances indeed. The distance in this case has to be > half the inter-particle distance, ~5 nm. They further propose that a difference in their work from earlier ones which show step nucleation [3] is that dimers and other pre-critical clusters have more chance of being formed and these clusters diffuse less readily and so transform into critical nucleii within a shorter surface hopping distance.

Perhaps the most important finding is that particle formation is not the simple process we might imagine. For the purposes of teaching and for clarity, we often imagine particles to be hemispheres which simply grow homogeneously, though we know that this cannot be true at the extremely small limit. Fujikawa et al. show that this is indeed far from the truth, in that the Ni particles tend to form monolayer islands very early in the growth process, which are of a small size (~1.5 nm), and at this stage the layer grows predominantly by forming new islands, not by growing old ones. Indeed, over the whole course of the experiment (a factor of ten change in coverage) there is essentially no change in island size. At a critical

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density of clusters the islands then transform into multilayer islands with a concomitant change in growth properties (e.g. the nucleation rate drops to a much lower value, and average height of the particles already formed increases linearly). There is a parallel with Goodman's work on the growth and reactivity of Au nanoparticles deposited on the same surface [7]. Here monolayer gold islands appear to be rather unreactive, whereas the double monolayer islands may have the best reactivity for low temperature CO oxidation, due to optimised electronic structure. If the growth process is similar, the optimum particles may be formed in a very specific time window of the growth process.

Returning to the question of the nucleation sites, it is not clear from Fujikawa's work what they are; it may well be that the nucleii are formed at defects on the terrace surface, as proposed by Wahlstrom et al. [5], and, indeed, such defects can be seen to be present in the some of the published images (e.g. Fig. 4b of Ref. [3]).

This work reiterates the incredible usefulness of STM, since, in principle, every particle in an area can be imaged and identified. There may be some problems with statistics in such a small imaged area, but nonetheless, Fujikawa et al. have shown that new insight into basic phenomena of the growth of anchored nanoparticles can be gained by this approach.

Important questions about the surface science of nanoparticles are being tackled and will be further addressed in the next few years. The biggest gaps in our knowledge which need to be filled include: resolution of the atomic structure of very small nanoparticles (probably requiring highly facetted particles), and the relationship to the structure of macroscopic crystals (especially surface reconstructions); the nature of the critical nucleus for growth; and, most importantly, direct measurement of the reactivity of nanoparticles and how metal-support interactions affect this behaviour.

References

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