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## Electrocatalysis at Single Nanoparticles

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# Summary

In this thesis catalysis at the nanometer scale is discussed. A catalyst is a substance that can enhance the speed of a chemical reaction, without being consumed in the process. While catalysts can be enzymes or acids, in this thesis only solid metal catalysts are discussed. It has been found that catalysts have a temporary, chemical, interaction with the reactants, and this chemical interaction is highly sensitive to the local shape of the catalyst and the atomic arrangement at the catalyst surface.

Metal catalysts are widely applied in industry, since they greatly increase the rate of chemical reactions in for instance the formation of gasoline from crude oil, or the production of plastics. Additionally, catalytic converters employ metals to reduce emissions from exhausts and are a standard fixture in contemporary automobiles. The metals in catalytic converters catalyse oxidation reactions, completing the combustion of carbon monoxide for instance. Such catalytic combustion can also be used to convert fuels to energy, in *fuel cells*, which have regained interest for application in remote electricity production, to power for instance cars or laptops. Nevertheless, the metals that show the highest efficiency for these reactions are noble metals such as platinum, which are rare and costly, and therefore these catalysts require research to maximize the per weight efficiency. The first step in reducing the mass of platinum required to power a car, is to maximize the surface area, which is done by dispersing the metal into ultrasmall nanoparticles. These characteristics of these nanoparticles have an impact on the catalytic activity, since, as described above, the arrangement of the surface atoms will depend on their size and shape.

The impact on catalytic activity of the size and shape of nanoparticles has been studied by analyzing dispersions of varying mean size. There can still appear size effects that remain hidden in the statistics of the size distribution, if the catalytic activity of a certain particle size or shape is dominant. Therefore it is interesting to attempt the study of individual nanoparticles.

Measuring a single nanoparticle is complicated by two major challenges: first the nanoparticle (with a diameter below 100nm, and more commonly in application, below 10nm) must be isolated in space and second the catalytic activity of the single particle must be accurately determined. The latter challenge can be met for a specific category of catalysis, namely electrocatalysis, which is the field of catalysis concerned with catalytic reactions that involve charge transfer at the interface between a solid catalyst and an electrolyte. The charge transfer as a result of a catalytic reactions can be measured as an electrical current, which is directly equivalent to the catalytic activity. Contemporary electronic amplifiers can amplify signals down to the femtoampère

range, which translates to tenths of thousands of electrons per second.

As discussed in chapter two, several techniques have emerged that combine ultrasensitive electronic measurement with nanometer scale resolution, to measure the chemical reactions at single catalyst nanoparticles. In this chapter various methods of nanoparticle manufacture are discussed, as well as classical methods of measuring the electrocatalytic activity of nanoparticles. Additionally, the current state-of-the-art of measurements on individual catalyst nanoparticles is detailed, with attention to the various methods of nanoparticle isolation.

Two of such methods have been used in the research described in this thesis and the distinguishing quality between them is the nature of the immobilization of the nanoparticles. One way to monitor the signal from a single particle is to create a very tiny 'landing platform' of an electrode, which has as its only function to conduct electrons to or from the catalyst particle, without generating a large signal of its own. Alternatively, the entire measurement system can be made on a scale approaching that of the NP. In electrochemical measurements, the size of the system is dictated by the charge conducting (often liquid) electrolyte. By confining the electrolyte to a droplet of nanoscopic dimensions, electrocatalysis on a very small area can be measured.

In chapter 3 the fabrication of nanoelectrodes small enough to measure single catalyst nanoparticles is presented. This fabrication occurs via the same techniques that are used to prepare transistors on computer processor chips, namely lithography. Using the extremely small tip of an electron beam, it is possible to etch out a nanoscale structure, facilitating the production of ultrasmall electrodes with surface area below a square micrometer. The geometrical surface area of the electrodes is verified using electron microscopy and by electrochemistry through the diffusion limited current of reversible redox couples.

These nanoelectrodes have been used to test the suitability of a specific manner of nanoparticle immobilization, which is the discrete detection of individual nanoparticles onto electrode surfaces. The detection method relies on the enhanced catalytic activity of the nanoparticles with respect to that of the electrode. As nanoparticles randomly move around a liquid electrolyte, that contains a fuel, they will start to oxidize that fuel upon contact with the electrode, which event appears as an electrical current. While it was found possible to detect the arrival of nanoparticles in such a way, through microscopic analysis it was found that the nanoparticles were aggregated into strings of particles. The source of aggregation was found to be the very fuel necessary for the detection of the particles. Therefore, this particular method is currently not suited for the immobilization of individual catalyst particles.

The alternative method used was the landing of particles onto a small electrode area inside an ultras-small electrolyte droplet, as mentioned above. The droplet exists at the end of a capillary, which is tapered to the miniscule diameter of a single micrometer. As the capillary is filled with an electrolyte, the droplet spontaneously forms at the end, the capillary forces being so large that the electrolyte cannot trickle out. The electrolyte contains a nanoparticles and a fuel in solution and the droplet is brought into contact with an inert electrode surface; as the nanoparticles contact that surface, their arrival is detected electronically. When a landing is detected the droplet is removed from the surface and a microscopical analysis of the surface is performed. In this way it was possible to correlate the amount of fuel combustion of a single particle to its size, and to measure the current-voltage diagram of a single NP for the first time.

These delicate measurements give an insight into the nature of analyzing individual catalyst nanoparticles and clearly show that it is feasible to determine their catalytic activity. Future measurements should reveal accurately the dependence of electrocatalysis on shape and size.

