

Direct observation of chemical reactions on single gold nanocrystals using surface plasmon spectroscopy

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Reaction rates of heterogeneous catalysis reactions are different for each individual catalyst particle. The rate depends on the morphology, size, crystal structure and composition of each catalyst nanoparticle. The *in-situ* measurement of reaction rates in catalysis is a challenging job for the researchers. Real-time monitoring of reaction rates on catalyst surface can be used to elucidate the exact reaction mechanism for catalysis. Gonzalez and Gates¹ have used time-resolved infra-red (IR) spectroscopy to study the oxidation of carbon monoxide on gold catalyst surfaces. However, they were not successful in correlating catalytic activity with nanocrystal structures, as they carried out ensemble average measurements.

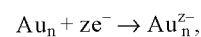
In 2008 scientists from the University of Melbourne, Australia used surface plasmon spectroscopy (SPS) to study chemical reactions on a single gold nanocrystal surface. Their findings were published in *Nature Nanotechnology*². Their results illustrate the first example of measuring the rate of redox catalysis *in-situ* on single nanocrystals. They studied nanoparticle-catalysed oxidative processes by combining dark-field microscopy and SPS. Gold nanorods were synthesized using the seed-mediated growth method developed by Nikoobakht and El-Sayed³. Gold decahedra and trigonal prisms were also synthesized using the seed-mediated growth method developed by Sanchez *et al.*⁴. It may be pointed out that the surface plasmon resonances of metal nanocrystals are sensitive to perturbations such as electron charging.

The microelectrode model of redox catalysis has been used to explain the nanoparticle-catalysed oxidation process. According to this model, a metal nanoparticle in solution couples two redox reactions by acting as electron reservoir. In the first step, a donor molecule transfers the electrons to the nanocrystal through

the following reaction: $D^- \rightarrow D + e^-$. In the next step, the electrons are transferred to the acceptor: $A + e^- \rightarrow A^-$.

The nanoparticle acts as a catalyst, if the rates of the above reactions are faster than the direct electron transfer from the donor, D^- to the acceptor. The SPS technique enabled them to detect the transferred electrons stored in a single catalyst nanoparticle and to quantify the concentration in real time. The stored electrons alter the plasma frequency of the metal, caused a blue shift in both the extinction and scattered spectra of the particle. Thus, they were able to monitor the steady-state charge on individual catalyst particle for the first time. Rayleigh scattering intensity is proportional to d^6 , where d is the diameter of the particle. Novo *et al.*² studied the gold-catalysed oxidation of ascorbic acid by dissolved oxygen. The direct electron transfer reaction is very slow in an aqueous solution. But electrons are transferred into gold nanoparticle catalyst by ascorbic acid. Oxygen discharge is slow due to the initial oxidation of ascorbic acid by any oxygen present in the solution, and the oxygen must diffuse back into the solution to pick up the stored electrons. This facilitates the build up of a large negative charge on the gold decahedron before oxygen reduction can compete and, consequently, the gold catalyst accumulates an enormous steady-state electron density. Rayleigh scattering spectra for a single gold nanocrystal were taken as a function of the reaction time. The scattering spectra were taken before and after the electron transfer by ascorbate ions (1, 2, 3 and 60 min after electron transfer). The SP band shifts ~ 20 nm during catalysis. A blue shift of the SP band was observed for more than 3 min as electrons were injected. Sixty minutes after electrons injection, the spectra shifted back to its original position.

On the basis of high-resolution transmission electron microscopy images, it is found that a single decahedron in this sample contains $\sim 1 \times 10^7$ gold atoms. This means that $\sim 8,30,000$ electrons would have to be added in 3 min. That is $\sim 4,600$ electrons per second can cause such a blue shift. As the gold decahedron becomes negatively charged, the injection rate would be expected to decrease and the rate of electron transfer from cathodically charged catalyst particle to oxygen will gradually increase. The red shift due to the reduction of oxygen to water corresponds to a consumption of 65 oxygen molecules per second. The overall mechanism is expressed by the following equation.



It is important to mention here that the sensitivity of the above measurement has limitation because of the intrinsic SP band shift per electron added by the current signal to noise collection efficiency of the CCD spectrometer.

It is expected that scientists would detect reactions of single molecules on catalyst nanocrystal surfaces and study the quantum reaction regimes, exhibiting the transfer of one electron at a time in the near future.

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4. Sanchez-Iglesias, A. *et al.*, *Adv. Mater.*, 2006, **18**, 2529–2534.

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