Silver clusters change form and color with each atom

Metal clusters are particles consisting of a few (usually between 2 and 100) metal atoms. Very often, metal clusters possess properties that differ markedly from both the constituting atoms and the bulk. Furthermore, they show nonscalable size dependence in their properties, that is, their properties vary with addition or removal of a single atom in a way that cannot be predicted. As a result, metal clusters provide chances and challenges. The possibility to tune the properties of materials by controlling the number of atoms is a great opportunity. Understanding their behavior in relation to their size and structure is, however, a scientific challenge.

Metal clusters are commonly fabricated in the gas phase in state-of-the-art research laboratories, and have been under intensive investigation now for more than 30 years. Metal clusters are mostly known for their unexpected catalytic activity. For instance, in contrast to gold atoms and bulk gold, gold clusters containing 8 gold atoms (Au_8) are highly active toward oxidation of carbon monoxide to carbon dioxide. Such unexpected catalytic activity originates from the specific electronic structure of the cluster, which can be probed with dedicated experiments. Since the optical properties of metal clusters (how they absorb and interact with light) can reveal their electronic structure in the most direct way, many research groups have been performing optical spectroscopic experiments on metal clusters. Among metal clusters, silver and gold clusters are especially attractive because their electrons can be excited to oscillate collectively with ultra-violet light. This collective oscillation of electrons is known as “plasmon” oscillation and leads to an enhanced light absorption- the so-called “plasmon resonance” which strongly contributes to the apparent color of gold and silver. The plasmon resonance is easily influenced by various parameters such as cluster’s size, cluster’s shape and cluster’s environment. The latter effect (dependence of plasmon resonance on the environment) makes silver clusters very suitable as chemical and biological sensors.

A common approach to study the properties of metal clusters is to deposit them onto a surface of a substrate to create supported metal cluster samples. One of the major challenges in exploring the optical properties of supported metal clusters in relation to their size, is due to the fact that each cluster size should be investigated in monodispersed samples, namely samples consisting of only a single size of clusters. Such samples therefore require a very low surface coverage (usually only ~0.1% of the surface is covered) and thus, a highly sensitive experimental method.
We have developed a suitable spectroscopic method to study the optical properties of supported metal clusters under controlled environmental conditions (ultra-high vacuum conditions having pressures about 10^{-10} mbar). This method is used to investigate the plasmon resonance of size-selected silver clusters of various sizes (Ag_n, n = 9, 15, 18, 21, 27, 35, 42, 45, and 55) fabricated at our lab. Our results reveal that the smaller the silver clusters get, the higher is the photon energy required to excite the plasmon resonance. However, this overall trend is superimposed by a nonscalable variation of the plasmon resonance, which has its origin in the geometrical shape of silver clusters, and thus gives insights about the shape variations of the clusters depending on their size.

Publication

Plasmons in supported size-selected silver nanoclusters.
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