1-2-4. Metal Nanoparticles

Overview

Metals exhibit interband transitions in the short-wavelength region, while at longer wavelengths they reflect light, giving rise to metallic luster. They have a high density of electronic states, contain free electrons, and exhibit electronic conduction. In metal nanoparticles (NPs), the oscillation of free electrons can resonate with the oscillating electric field of light, giving rise to localized surface plasmon resonance (LSPR). LSPR generates an optical near field around the particle, which can excite dyes or semiconductors nearby. In the relaxation process of LSPR, energetic (or hot) electron–hole pairs are generated, leading to charge separation and redox reactions.

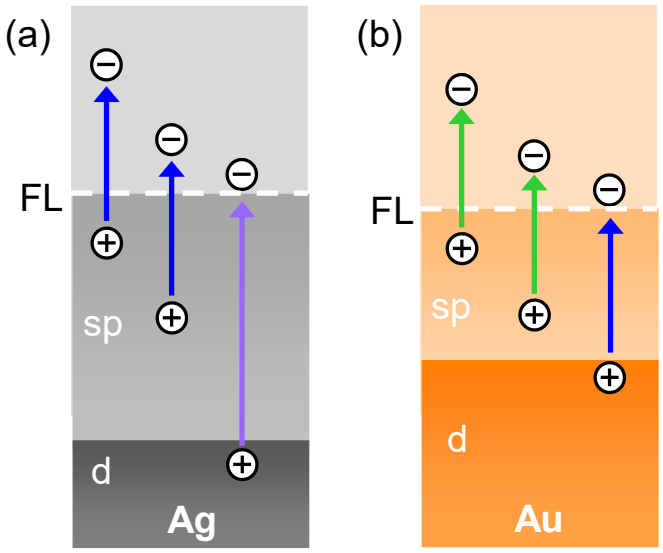

Figure 1. Excitation of electrons in (a) Ag and (b) Au NPs.

Current Status and Frontiers

Metal clusters possess discrete electronic structures with low densities of states. As their size increases to one nanometer or more, the energy spacing between bands narrows, and the structure becomes continuous. At this point, the quantum size effect vanishes, and the system begins to resemble bulk metals. Because of the high density of electronic states, electrons can be thermally excited even at room temperature, producing free electrons and enabling electronic conduction. These electronic properties are thus common to NPs of this size and to bulk metals.

Metals absorb light through interband transitions in the short-wavelength region. At longer wavelengths, bulk metals reflect light at their surfaces, whereas NPs on the order of a few to several hundred nanometers absorb light through LSPR.

For example, in Ag (Fig. 1a), interband excitation occurs from the d-band to the sp-band in the ultraviolet region. Small spherical Ag NPs with diameters of a few to ~10 nm exhibit LSPR around 400 nm. Relaxation of the LSPR leads to intraband excitation within the sp-band.[1] As illustrated, excitation can occur from relatively deep or shallower levels.

In the case of Au NPs (Fig. 1b), interband absorption extends from the ultraviolet into the visible region. Small spherical Au NPs exhibit LSPR around 520 nm.

As NP size increases, the LSPR wavelength gradually red-shifts. Stronger anisotropy in particle shape leads to even larger red-shifts. For instance, in Ag or Au nanorods, an increase in aspect ratio shifts the LSPR wavelength of the longitudinal mode (electron oscillation along the long axis) into the near-infrared region. Because LSPR also red-shifts with increasing refractive index of the surrounding medium, adsorption of chemical species based on local chemical interactions can be monitored. This principle underlies LSPR sensors, which are applied in chemical and biosensing.

LSPR is not limited to metals such as Au, Ag, and Cu; it can also be observed in compound NPs such as indium tin oxide (ITO), provided the carrier density and mobility are sufficiently high (Teranishi et al.).[2]

LSPR produces optical near fields (localized oscillating electric fields) around metal NPs, which can excite nearby dyes or semiconductors as energy transfer in a broad sense.

The hot electron–hole pairs generated during LSPR relaxation usually undergo thermal deactivation. However, if they are separated, they can be harnessed for chemical reactions. For example, when Ag nanoplates are irradiated at their LSPR wavelength, growth of the nanoplates has been observed.[3] Similarly, irradiation of Au nanocubes with circularly polarized light while depositing Ag produces chiral Au–Ag composite NPs that exhibit circular dichroism (CD) (Tatsuma et al.).[4] By transferring either electrons, holes, or both to semiconductors or other acceptors, the charge-separated state can be prolonged, allowing more efficient utilization in reactions (see Section "2-4-1. Plasmon-Induced Charge Separation").

References

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Future Perspectives and Directions

Challenges and goals for the next decade: Sustaining the excited states of metal NPs and applying them to chemical reactions.

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