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Designing Plasmon Resonances

The optical resonances of metal nanoparticles, which are known as localized surface plasmon resonances (LSPRs), have a long history on physical chemistry, dating back to Faraday's studies in the 1850s.¹ They are still a topic of great interest, with current research focusing on sensing applications,² increasing absorption in photovoltaic devices,^{3,4} and surface-enhanced spectroscopies.^{5,6} The LSPR corresponds to a coherent oscillation of the conduction electrons of the particle, and the position depends on the dielectric constants and the size and shape of the particle,⁷ as well as the dielectric constant of the medium.² For nanoparticles of noble metals (silver and gold), the LSPRs appear in the visible region of the spectrum.⁷ Using a simple model for the dielectric constants of metals, it can be shown that the LSPR frequency is proportional to the square root of the electron density in the metal.⁸ As this quantity is similar for silver and gold, their LSPRs appear in the same spectral region. The LSPR frequency can be shifted by adding electrons to the particles;⁹ however, because the electron density of metals is already high, the shifts are relatively small.¹⁰

In recent years, several groups have demonstrated that doped semiconductor nanoparticles can also show surface plasmon resonances.^{11–13} These materials have low conduction electron densities; thus, their LSPRs occur in the mid-IR to near-IR region. Importantly, by controlling the doping and, therefore, the electron density in the particle, the position of the LSPR can be tuned. The Perspectives by Lounis et al.¹⁴ and Fauchaux et al.¹⁵ discuss different aspects of the physical chemistry of doped semiconductor nanoparticles. Free electrons can be created in semiconductors in a variety of ways, for example, by creating vacancies in the lattice, such as in the $C_{2-x}S$ system,^{11–13} introducing dopant atoms into the nanoparticle,¹⁶ or by chemical or photochemical reduction.^{17–19} Indeed, a combination of these effects allows the LSPR to be turned on and off.¹⁴ Like what happens with metallic nanoparticles, the shape of the particle is also important in determining the position of the LSPR in doped semiconductors, and a number of studies have been performed on different shaped structures,^{16,20} in addition to spherical particles.

An important aspect that is highlighted in both Perspectives is the need to develop an accurate physical model for the optical properties of doped semiconductors.^{14,15} The starting point in understanding the properties of these materials is the venerable Drude model.⁸ However, recent work has shown that this model is not adequate at small sizes for doped semiconductors.²¹ Accurate modeling of the optical properties of metal nanoparticles can be achieved by using the measured dielectric constants of the metal.²² Unfortunately, this is not feasible for doped semiconductor materials because different doping densities create what is essentially a new material. In order to develop a better description of the dielectric constants of doped semiconductors, more work is needed to understand the limitations of the current theories²³ and to describe processes such as electron scattering.^{14,15}

Although this is a relatively new area of research, there has been rapid progress in developing methods to control the doping in semiconductor nanoparticles, as well as in finding new semiconductor materials that can be used to support surface plasmon resonances. However, a lot remains to be done. There are a number of challenges in the synthesis of these materials,²⁴ the theoretical descriptions of their dielectric constants,^{21,23} and in understanding their photophysics.²⁵ These challenges will make this an exciting area of science to work in in the coming years.

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Notes

Views expressed in this Editorial are those of the author and not necessarily the views of the ACS.

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