



Comment

Recycling scattered light for energy conversion

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Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy mario.pagliaro@cnr.it Light and its applications permeate many fields, including chemistry, physics, medicine, and the nature of light makes it an ideal information and energy carrier. Aiming to take better advantage of this potential, many researchers are devoted to understanding how to effectively manipulate light for specific purposes.

Inspired by the pioneering work from Gustav Mie in 1908, it has been recognized that metal nanoparticles are able to tune light through the interaction of free electrons in metals with photons. This attractive capacity of metal nanostructures has been under scientific scrutiny for over a century, culminating in the niche



A new optical absorption model of small Pt nanoparticles for solar energy conversion.

application of their surface plasmons (SPs), as typically exemplified by the broad technological and scientific applications of Au and Ag nanostructures. In sharp contrast, the utilization of Pt nanoparticles for light harvesting remains quite limited, because (i) small (<10 nm) Pt nanoparticles with high surface-to-volume ratio always fail to exhibit SP resonance absorption peaks in the range of wavelength over 200 nm, and thus (ii) the SP excitation of Pt nanoparticles often needs much higher photon energy than that for Au or Ag of the same size. The challenge of rationally tuning the optical absorption peaks of small (<10 nm) Pt nanoparticles as well as saving the photon energy for electron excitation has remained a scientific mystery.

Writing in Nature Photonics, a team led by Yi-Jun Xu at Fuzhou University (China), Yugang Sun at Temple University (US) and their co-workers have taken a significant step toward rising to this challenge. They have developed a new optical absorption model to identify the absorption peak of supported Pt nanoparticles in the visible light region by adjusting their dielectric environment through controlled nanostructure design instead of increasing the size of the Pt nanoparticles. The researchers found that the localized absorption peak of Pt nanoparticles can be further tuned to the longer visible wavelength region either by simply increasing the diameter of spherical SiO₂ supports or by fine-coating the Pt nanoparticles with a thin shell of the semiconductor TiO₂.

The theoretical modeling results by both Mie theory and finitedifference time-domain (FDTD) method reveal that the supported Pt nanoparticles are able to absorb scattered light in the near field of dielectric surface of the SiO_2 spheres, thereby exhibiting distinct absorption peaks correlated to the Mie scattering resonances of the SiO_2 supports. The obvious redshift of the scattering and absorption peaks of the composites after coating the thin TiO₂ dielectric shell is induced by the larger refractive index of TiO₂. The observed localized absorption of the supported Pt nanoparticles have proven to endow the Pt/SiO₂@TiO₂ core-shell composites with visible-light ($\lambda > 500$ nm) photoactivity toward various reactions, including selective oxidation of alcohols, selective reduction of aromatic nitro compounds and hydrogen evolution from water splitting.

Owing to the clear identification of the localized absorption peaks of Pt nanoparticles which provides a basic prerequisite for studying their definite contribution to the photoactivity enhancement of the composites, the action spectrum analysis has evidenced that the photoredox processes are enabled by the light absorption and photoexcitation of Pt nanoparticles.

On the basis of this newly-demonstrated optical model, there are even more intriguing questions to be explored and inspiration to be drawn. For example, how would the morphology/microstructure of the supports affect the spectral control of Pt nanoparticles? Can such light absorption model be extended to tuning the optical properties of other metal nanostructures? If the metal nanostructures are surrounded by multiple electric fields from different lights, such as the incident light, the scattered light, as well as the near-field coupling or far-field dipolar interaction among the metal nanostructures, will these overlapped electromagnetic fields lead to new optical observations?

Answers to these open questions deserve more research effort, but a new vista for utilizing metal nanoparticles as visible-light photon absorbers to recycle the scattered light for solar energy conversion has been opened.

Further reading

N. Zhang, et al. Nat. Photonics 10 (2016) 473, 10.1038/nphoton.2016.76.