Quantum-sized metal nanoparticles: Bridging photons and chemical transformations

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The incompatibility of the energy of a solar photon and the absorption band of a chemical bond prevents the use of light to activate the chemical bond for interesting chemical reactions directly. This presentation will focus on a strategy that enables the efficient coupling of photon energy into chemical bonds to selectively promote the desired chemical reactions. The strategy relies on the generation of hot electrons in quantum-sized metal nanoparticles (QSMNPs, with size < 10 nm) upon photo-illumination and the next efficient injection of the hot electrons into specific chemical bonds. The redistribution of hot electrons in the chemical bonds dissipates the kinetic energy of hot electrons to the chemical bonds, activating the chemical bonds to promote the target chemical reactions. These sequential processes occur in a confined space, representing a series of quantum transitions, i) optical-to-electronic transition in quantum-sized metal nanoparticles (i.e., hot electron generation), ii) electronic-to-electrical transition at the nanoparticle/adsorbate interface (i.e., hot electron injection), and iii) electrical-to-electronic transition in adsorbate molecules (i.e., chemical bond activation). These transition processes are summarized in Figure 1.

Selective oxidation of alcohols to aldehydes rather than ketones/ acids, a class of important chemical reactions for many industrial processes (e.g., esterification), will be used as an example to highlight the use of QSMNPs for photo-driven selective chemical transformation on platinum group metal (PMG) nanoparticle catalysts, which do not exhibit strong optical absorption. Current practices primarily rely on the use of strong oxidants (e.g., permanganate and dichromate), which are too strong in oxidizing power to prevent over-oxidation of alcohols to ketones. These strong oxidants are usually toxic and have to be removed from the products. In contrast, using ambient oxygen as oxidant is promising to develop an environmentally friendly synthesis strategy that does not require additional separation. However, ambient oxygen is lack of the power to oxidize alcohols at mild temperatures. Therefore, precisely controlling the oxidizing power of the oxidants becomes crucial to promote the selective oxidation of alcohols to aldehydes. The PMG QSMNPs are used to improve the selective oxidation with ambient oxygen by converting the molecular oxygen adsorbed on the catalyst to more active species when the QSMNPs absorb visible light.

Figure 1. Schematic illustration of multiple quantum transition processes involved in hot-electron-driven chemical transformation on photo-excited quantum-sized metal catalyst nanoparticles.