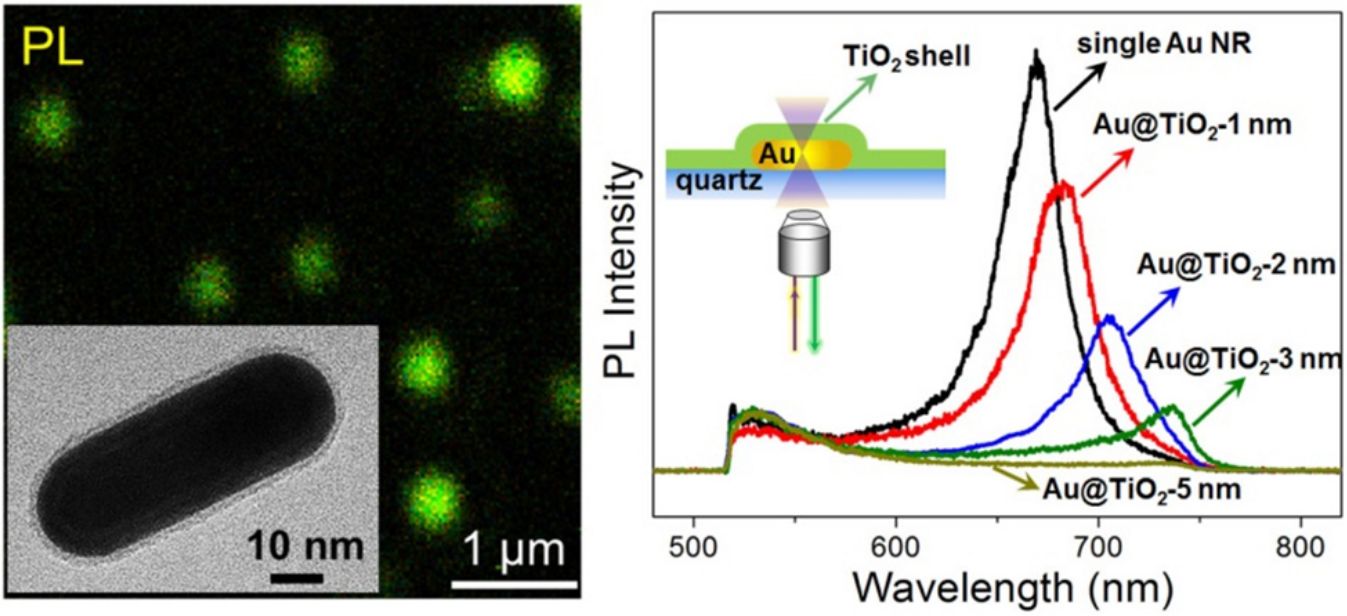
The “luminous” gold nanorod: direct observation of electron transfer

Photoluminescence (PL), in which photon is emitted after the absorption of another photon, has been important for many technologies. The first observation of visible PL of gold dates back to 1969, when Mooradian studied bulk gold and observed a broad luminescence spectrum, understandably, the efficiency is very low. Later, people found that the gold nanoparticles show highly enhanced visible PL by several orders of magnitude compared with bulk gold. Among the gold nanoparticles, gold nanorods exhibit the highest PL property.



Early efforts to understand the emission from gold nanoparticles have relied on ensemble measurements. However, the chemical synthesis of metal nanostructures often yields a broad distribution of sizes, shapes, and constituents. Thus, single-particle analyses are essential to exclude undesirable effects caused by sample heterogeneity and impurities.

Considering that the PL of gold nanorods is sensitive to the interfacial electron transfer between gold and its surroundings, it can be employed as an efficient nano-probe for the electron transfer process. Up to date, the efficient conversion of solar energy to electric or chemical energy by semiconductors has become a common concern in the world. Among them, titanium dioxide (TiO_2) has been extensively studied due to its advantages such as non-toxic, chemical stability, and low-cost et al. Generally, gold nanoparticles were combined with TiO_2 to enhance its photoelectric performance. However, the spatial-related interfacial electron transfer mechanism was rarely reported. Here, we developed a novel sensing method for monitoring of electron transfer between single gold nanorod and TiO_2 by utilizing the PL of gold nanorod. Notably, homogeneous coating of

TiO_2 on gold nanorods with precisely controllable shell thickness is very essential, because the electron transfer is sensitive to the shell thickness even at sub-nanometer level. Atomic layer deposition (ALD) helped us to obtain this goal.

Single-particle PL measurements were carried out with a 485 nm laser. The figure at left shows a typical PL image of gold nanorods dispersed on quartz cover glass. Each bright dot represents the PL from each gold nanorod. A strong PL peak was observed in the PL spectrum for naked gold nanorod. When the surface of gold nanorods was coated by TiO_2, the PL intensities of these TiO_2-coated gold nanorods dramatically decreased as increasing the thickness of TiO_2. When the thickness of the TiO_2 shell increased to 5 nm, the PL was almost totally quenched, that means, the gold nanorods became “nonluminous”.

When gold nanorods were coated with a layer of TiO_2, the hot electrons can transfer from gold nanorods to the TiO_2 shell, which competes with the light-emission and hence gives rise to the PL damping. The enhanced quenching effect with increasing the thickness of TiO_2 indicates a more efficient electron transfer from Au to TiO_2. Therefore, we can observe the invisible electron transfer process by monitoring the visible PL change of gold nanorods. The PL from gold nanorods can be employed as an efficient detector for the electron transfer in other systems.

Publication

Plasmon-induced spatial electron transfer between single Au nanorods and ALD-coated TiO2: dependence on TiO2 thickness.
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