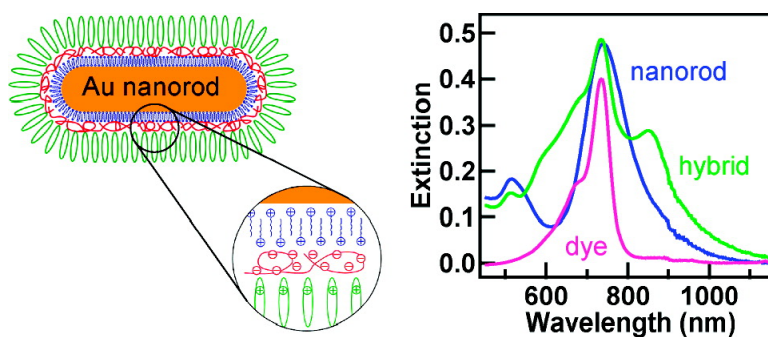


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Coupling between Molecular and Plasmonic Resonances in Freestanding Dye–Gold Nanorod Hybrid Nanostructures

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The effect of dye molecules on the plasmon properties of metal films and nanoparticles has been attracting increasing attention. The formation of hybrid materials between inorganic templates and organic dyes and understanding of their interactions can lead to the development of optical devices with functionalities such as switching,¹ lasing,² energy transfer,³ and sensing.⁴ Coupling between the plasmon of metal nanoparticles and molecular resonance of adsorbed dyes has been observed.^{5–7} The coupling strength is found to be strongly dependent on the spectral overlap between the molecular and plasmonic resonances. Metal nanoparticles employed in previous experiments are attached on substrates, which makes it difficult to coat dyes uniformly around each nanoparticle and thus causes difficulty in comparing experimental results with theoretical predictions.^{8,9}

In this work, we report on the construction of freestanding hybrid nanostructures between dyes and colloidal Au nanorods (Figure 1A) and the resonance coupling between the localized plasmon of nanorods and adsorbed dyes. The coupling strength is tuned by using nanorods with longitudinal plasmon wavelengths varying from 570 to 870 nm. The maximum coupling-induced plasmon shift is observed to be larger than 120 nm, about 2–4 times that obtained previously.^{5–7} The plasmon shift is found to decay rapidly with increasing spacing between the dye and nanorod. We further demonstrate that the resonance coupling can be switched off by photodecomposing adsorbed dyes.

Gold nanorods of varying longitudinal plasmon wavelengths were grown using the previously reported transverse overgrowth method¹⁰ (see Supporting Information (SI) for growth details and Figure S2 for transmission electron microscopy (TEM) images of representative nanorod samples). The resulting nanorods are stabilized in aqueous 0.1 M cetyltrimethylammonium bromide (CTAB) solutions and positively charged. The nanorod concentrations of all the samples were adjusted to 0.9 nM according to previously measured extinction coefficients.¹¹ A dye, HITC (CAS No. 16595-48-5, Figure 1A), carrying a positive charge, was employed. It has a major absorption peak at 734 nm and a minor peak at 670 nm (Figure 1B). A layer-by-layer assembly method, modified from that developed for coating silica on Au nanorods,¹² was used to make HITC–nanorod hybrid nanostructures. Briefly, 2 mL of each nanorod sample was centrifuged at 6300g for 15 min. The precipitate was redispersed in 2 mL of deionized water and subsequently added dropwise to 2 mL of poly(sodium 4-styrenesulfonate) (PSS, MW 70 000, 2 g/L, 6 mM NaCl) under vigorous stirring. The mixture was stirred for 3 h, centrifuged, and then redispersed in 2 mL of water to give negatively charged PSS-coated nanorod samples, denoted by Au@PSS. The hybrid nanostructures were prepared by mixing together 200 μ L of each Au@PSS sample, 700 μ L of water, and 100 μ L of an aqueous 100 μ M HITC solution. Each mixture was kept undisturbed overnight, centrifuged to remove unadsorbed HITC, and then redispersed in 1 mL of water.

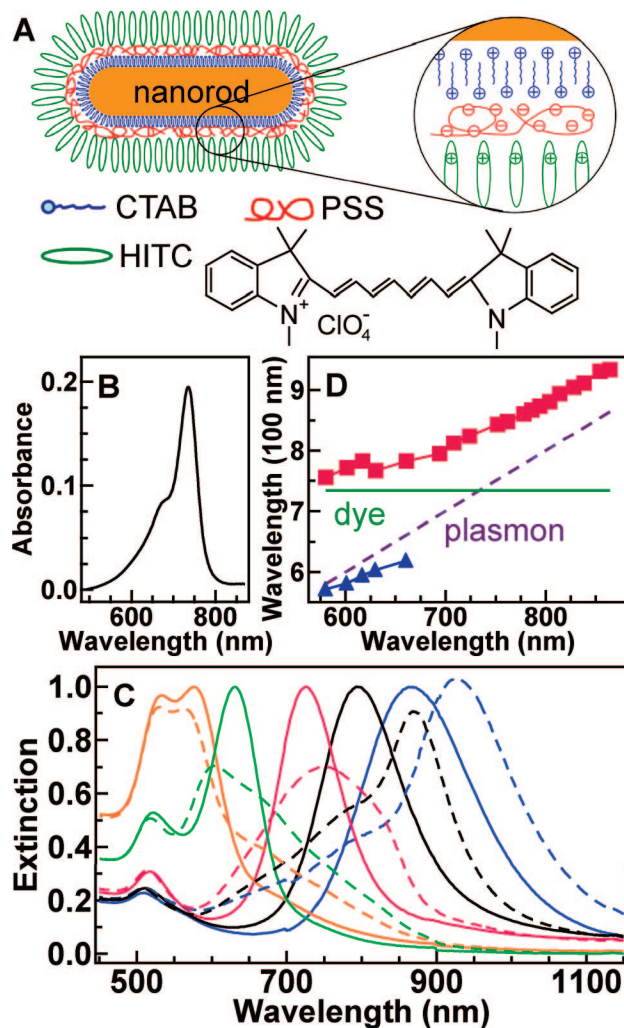


Figure 1. (A) Schematic HITC–Au nanorod hybrid nanostructure. (B) Absorption spectrum of 10 μ M HITC. (C) Extinction spectra of Au@PSS samples (solid lines) and corresponding Au@PSS/HITC samples (dashed lines, drawn in the same color). The extinction spectra of Au@PSS samples have been normalized against the longitudinal plasmon peak intensities, and those of Au@PSS/HITC samples have been first scaled to the same nanorod concentration and then normalized against the longitudinal plasmon peak intensities of the corresponding Au@PSS samples. (D) Energy diagram of the resonance coupling (red and blue). The presence of the minor absorption peak of HITC precludes the extraction of a complete high-energy branch (blue) by curve fitting.

HITC–nanorod nanostructures exhibit clearly different colors from corresponding Au@PSS samples (Figure S3 in SI). Compared with the extinction spectra of Au@PSS samples, those of Au@PSS/HITC samples reveal the splitting of the longitudinal plasmon peaks into two resonance peaks (Figure 1C and Figures S4–S6 in SI),

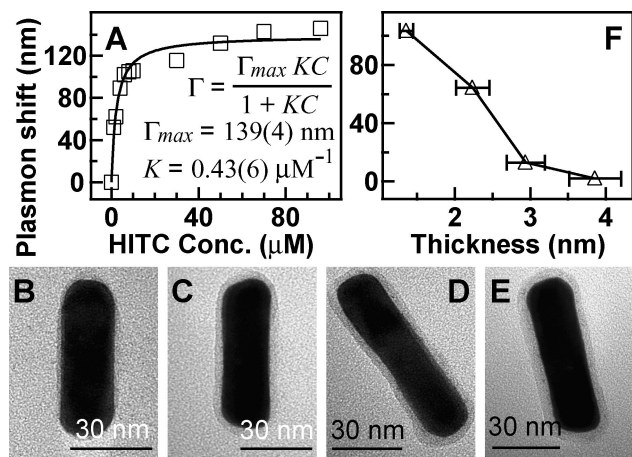


Figure 2. (A) Dependence of the plasmon shift on the concentration of HITC. The nanorod concentration is 0.18 nM. The line is a fit according to the Langmuir equation, $\Gamma(\text{max}) = (\text{maximum})$ plasmon shift. $K = \text{Langmuir equilibrium constant}$. $C = \text{HITC concentration}$. (B–E) TEM images of Au@PSS/PAH_nPSS nanostructures with $n = 0–3$, respectively. (F) Dependence of the plasmon shift on the thickness of polyelectrolyte coating. The error bars represent the standard deviation of the thickness. The plasmon wavelengths of the Au@PSS sample in (A) and the CTAB-stabilized nanorods in (B) are both 740 nm.

suggesting the coupling between the molecular and plasmonic resonances. The peak position and intensity vary systematically as a function of the separation between the two original resonance peaks. When the longitudinal plasmon is far away from the dye resonance on either side, it splits into a strong peak that is shifted further away from the dye resonance and a weak peak on the other side. When the plasmon is close to the dye resonance, the split peaks exhibit comparable intensities. The wavelengths of the split peaks were extracted by fitting the extinction spectra with Lorentzian peaks (Figure S7 in SI) and plotted versus the plasmon wavelengths for a total of 19 Au@PSS samples (Figure 1D). The anticrossing behavior of the molecular and plasmonic resonances is clearly observed, which is in agreement with what has been theoretically predicted.⁹

The resonance coupling-induced plasmon splitting is found to be dependent on the concentration of HITC (Figure S8 in SI). Figure 2A shows the concentration dependence of the plasmon shift. There exists a clear transition point around 8 μM. Below 8 μM, the plasmon shift rises rapidly. Above 8 μM, it increases slowly and becomes saturated at high concentrations of HITC. At the transition point, the amount of HITC adsorbed on the surface of Au@PSS particles is probably one monolayer, corresponding to ~44 000 dye molecules per nanorod. This amount is also consistent with that determined by absorption measurements, where 21% of 10 μM HITC is found to be left in the supernatant after the precipitation of hybrid nanostructures by centrifugation (Figure S9 in SI). Moreover, the concentration dependence of the plasmon shift can be fitted with the Langmuir equation, giving a maximum shift of 139 nm and a binding constant of 0.43 μM⁻¹.

The plasmon shift is also strongly dependent on the spacing between the dye and nanorod. Positively charged poly(allylamine hydrochloride) (PAH, MW 15 000, 2 g/L, 6 mM NaCl) was used together with PSS to coat multiple layers of oppositely charged polyelectrolytes on nanorods. The coating thicknesses measured from TEM images (Figure 2B–E) are 1.4 (2), 2.2 (4), 2.9 (5), and 3.9 (7) nm for the Au@PSS/PAH_nPSS ($n = 0–3$) samples. As the dye–nanorod spacing is increased from 1.4 to 3.9 nm, the plasmon shift drops quickly to 0 (Figure 2F and Figure S10 in SI), suggesting the disappearance of the resonance coupling.

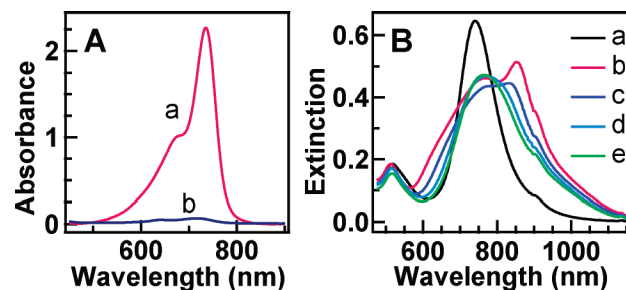


Figure 3. (A) Absorption spectra of 10 mM HITC before (a) and after (b) laser illumination at 457 nm and 80 mW for 6 h. (B) Extinction spectra of (a) Au@PSS sample (plasmon wavelength at 740 nm), (b) the sample adsorbed with HITC, and (c–e) the Au@PSS/HITC sample after laser illumination for 2, 4, and 6 h, respectively. The remaining plasmon shift (24 nm) is probably caused by the photodecomposed dye molecules acting as a dielectric coating layer.

The resonance coupling can be switched off by decomposing the dye molecules adsorbed on Au nanorods. As an example, HITC can be photodecomposed by laser illumination at 457 nm (Figure 3A and Figure S11 in SI). The plasmon shift induced by the resonance coupling between HITC molecules and nanorods is seen to decrease gradually upon laser illumination (Figure 3B).

We have further prepared hybrid nanostructures using rhodamine 590 and rhodamine 640 and found that the maximum plasmon shift is 15 and 34 nm for the former and latter, respectively (Figures S12–S14 in SI). The different plasmon shifts could be due to the differences in the transition dipole strength and orientation, molecular size, and packing density for the different dyes.⁹ More systematic studies are required to understand the effect of dye properties on the resonance coupling.

In conclusion, we have constructed hybrid nanostructures of dyes and colloidal Au nanorods. The anticrossing of the molecular and plasmonic resonances has been observed. The coupling-induced plasmon shift is strongly dependent on the dye concentration and the spacing between dyes and nanorods. These freestanding nanostructures will be particularly useful for sensing applications where sensing agents are required to be delivered to specific locations for interaction with targets.

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Supporting Information Available: Au nanorod growth, extinction spectra, TEM images, and digital pictures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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