Photoluminescence enhancement in CdS nanoparticles by surface-plasmon resonance

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To examine the influence of metal nanoparticles on the photoluminescence of semiconductors, colloidal mixtures of CdS and Au nanoparticles were prepared with different CdS/Au fractions. Compared to the cadmium-sulfide nanocrystals (quantum efficiency $\approx 7\%$), the CdS/Au mixtures showed enhanced luminescence properties (quantum efficiency $\approx 14\%$). The existence of an optimum ratio of metal to semiconductor nanoparticles for the photoluminescence intensity indicates that interactions between the metal and semiconductor nanoparticles induced by surface-plasmon resonance occur constructively at appropriate distances. © 2011 American Institute of Physics. [doi:10.1063/1.3615782]

Recently, there have been many studies on surface-plasmon induced local-field enhancements. The optical properties of fluorescent semiconductors located near a metal nanoparticle are affected by the surface-plasmon resonance. It is believed that when the surface-plasmon energy of the metal matches the luminescent photon energy of the semiconductor nanoparticles, the resulting resonance can lead to an effective energy transfer between the metal surface and the luminescent nanoparticles. This induces the enhancement or quenching of the fluorescence, depending on the distance between the semiconductor and the metal surface. In the case of luminescent nanoparticles located at very short distances from a metal surface, nonradiative energy transfer to the surface plasmon in the metal takes place. The electromagnetic-field enhancement due to surface-plasmon resonance, however, still occurs at longer distances from the metal nanoparticle. As a result, there is an optimal distance from the semiconductor to the metal surface for the enhancement of the photoluminescence (PL).

The interaction between fluorescent nanomaterials and metallic nanostructured surfaces is an interesting subject in nanoscience, and its study provides insight into the basic aspects of field-matter interactions. Geddes’ group developed silver core-silica shell nanoparticles with various shell thicknesses featuring a variety of fluorophores to show the existence of an optimum distance between the metal nanoparticles and fluorescent materials for the PL intensity. In another study, Artemyev’s group investigated the enhancement of the luminescence of CdSe/ZnS core/shell quantum dots on gold colloids as a function of the semiconductor–metal distance. Okamoto’s group examined the effect of the surface-plasmon resonance on the photoluminescence of CdS/Au mole fractions (10:0, 10:0.5, 10:1, 10:2, or 10:4). CdS/Au nanoparticles were synthesized using a liquid-solid-solution method to prepare nearly monodispersed nanoparticles. Cadmium chloride (CdCl$_2$, 0.182 g) and sodium sulfide (Na$_2$S, 0.078 g) were separately dissolved in distilled water (15 ml) and stirred to achieve their complete dissolution. The cadmium chloride solution was placed into an autoclave followed by the addition of the sodium sulfide solution. Sodium linoleate ((C$_{17}$H$_{31}$)COONa, 0.1 g) and linoleic acid ((C$_{17}$H$_{31}$)COOH, 0.2 ml) dissolved in ethanol were added to the resulting solution to control the reaction rate. The autoclave was sealed and heated at 100°C for 12 h. The resulting mixture was centrifuged, cleaned several times with ethanol, and dried at 60°C for 5 h. After their synthesis, the CdS nanoparticles were dispersed in CHCl$_3$.

To synthesize the Au nanoparticles, gold chloride trihydrate (HAuCl$_4$·3H$_2$O, 0.196 g) was dissolved in distilled water (20 ml). Sodium linoleate ((C$_{17}$H$_{31}$)COONa, 0.1 g) and linoleic acid ((C$_{17}$H$_{31}$)COOH, 0.2 ml) dissolved in ethanol were then added, and the autoclave was heated at 50°C for 10 h. The resulting mixture was centrifuged, cleaned several times with ethanol, and dried at 60°C for 5 h. After their synthesis, the Au nanoparticles were added to the colloidal CdS nanoparticles dispersed in CHCl$_3$, with various CdS/Au mole fractions (10:0, 10:0.5, 10:1, 10:2, or 10:4). The CdS nanoparticles are located within 117, 93, 74, and 59 nm of the circumference of the Au nanoparticles for CdS/Au mole fractions of 10:0.5, 10:1, 10:2, or 10:4, respectively.

The nanostructures of the CdS and Au nanoparticles were analyzed by x-ray diffraction (XRD, M18XHF-SRA, MAC Science). The PL spectra were measured using a spectrofluorometer (FP-6500, JASCO) with a Xe lamp, and the absorption spectra were recorded on a UV/vis spectrophotometer (Lambda 20, Perkin-Elmer). The time-resolved PL spectra were measured using a time-correlated single-photon counting system.

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decay curves were measured using a picosecond laser system (TR-PL, FLS920P, Edinburgh).

The x-ray diffraction patterns of the CdS and Au nanoparticles were measured, as shown in Fig. S1 (see Ref. 19). The CdS and Au nanoparticles exhibited cubic zinc-blende and face-centered cubic structures, respectively, and there were no secondary phases in the nanocrystals. The nanoparticle sizes were estimated from the Scherrer equation of $D_k$ vs. $k$ (the scattering vector $k = (4\pi/\lambda)s\sin(\theta)$). The three peaks were fitted using a double-peak Lorentzian function for $K_{21}$ and $K_{22}$ (Refs. 15, 16, 20, and 21).

The photoluminescence emission spectra of the mixed CdS/Au nanoparticles were measured with 400 nm excitation at room temperature (Fig. 1). The broad emission peak at $\sim$540 nm and shoulder peak at $\sim$600 nm were attributed to the band-edge and surface-defect transition of the CdS nanoparticles, respectively.22 The PL intensities improved with increasing gold fraction of the semiconductor/metal mixture, and a mole fraction of 10:1 resulted in the strongest emission peak. However, a decrease in the luminescence intensity was observed at higher Au fractions, indicating the existence of an optimum resonance distance between the metal and semiconductor for the luminescence.

Figure S2 (see Ref. 19) shows the absorption spectra of the mixed CdS/Au nanoparticles. The pure Au nanoparticles in CHCl$_3$ showed a surface-plasmon peak at $\sim$550 nm, corresponding to a particle size of 22 nm as measured by x-ray diffraction.23 It can be seen that the surface-plasmon peak matches well with the CdS luminescence. No significant surface-plasmon peak of the Au nanoparticles was observed in the spectra of the CdS/Au mixtures, probably due to the saturated absorbance of the highly concentrated semiconductor nanoparticles. Quantum efficiencies were measured in dilute samples to avoid experimental errors typically caused by re-excitation and trapping of emission, as shown in Fig. S4 (Ref. 24). To examine the luminescence properties quantitatively, the quantum efficiencies of the colloidal CdS/Au mixtures were estimated using Rhodamine 6G in ethanol (a quantum efficiency of approximately 95% for an excitation wavelength of 480 nm). Though comparing their absor-

![FIG. 1. (Color online) Photoluminescence spectra of mixed CdS/Au nanoparticles with various CdS/Au mole fractions.](image1)

![FIG. 2. (Color online) Decay curves of the CdS/Au mixtures as a function of the mole fraction, along with the corresponding decay time ($\tau$). The samples were excited at 400 nm and recorded at an emission wavelength of 540 nm. The laser pulse is shown as a dotted line.)](image2)

![FIG. 3. (Color online) Quantum efficiency, radiative recombination rate, and nonradiative recombination rate of the CdS/Au mixtures with various mole fractions. The estimated quantum efficiency is also shown ($\times$ symbol.)](image3)

bances with Rhodamine 6G may lead to limited accuracy, an indirect method was adopted for experimental convenience.25–27 In Fig. S2(c), the CdS/Au mixtures exhibited lower reflectance than the bare CdS nanoparticles, and this result indicates that the stronger PL intensity of CdS/Au mixtures is attributed to surface-plasmon resonance rather than scattering by Au nanoparticles.28

Time-resolved photoluminescence measurements were performed to determine the carrier dynamics in the nanoparticle mixture, as shown in Fig. 2. The decay curves were analyzed in terms of the radiative/nonradiative recombination rates, using the equation $k_{\text{total}} = k_{\text{rad}} + k_{\text{nonrad}}$ where $k_{\text{total}}$, $k_{\text{rad}}$, and $k_{\text{nonrad}}$ are the total, radiative, and nonradiative recombination rates, respectively. The quantum efficiency ($\eta$) is the ratio of the radiative recombination to the total recombination as follows:

$$\eta = \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{nonrad}}} = k_{\text{rad}} \times \tau,$$

where the decay time ($\tau = (k_{\text{total}})^{-1}$) was obtained from a single-exponential fitting of the PL decay curve.

Figure 3 shows the quantum efficiencies and radiative/nonradiative recombination rates of the CdS/Au mixtures with various mole fractions. There are obvious correlations between the quantum efficiency and radiative recombination rate. The radiative recombination rate was proportional to the quantum efficiency, indicating that the increase of the
radiative recombination rate by the surface-plasmon resonance is the main reason for the enhancement of the quantum efficiency. However, a decrease in the radiative recombination rate was observed at higher Au fractions, because nonradiative recombination occurs when a metal is in close proximity to other metals (within 140 nm) due to the resulting destructive interference of the surface plasmons.

A possible mechanism of the surface plasmon-exciton coupling is proposed in Fig. 4. If there are no Au nanoparticles around the CdS nanoparticles dispersed in CHCl₃, nonradiative recombination is dominant. However, when the Au nanoparticles are at a moderate distance (10–70 nm) from the CdS nanoparticles, and the emission energy of the CdS nanoparticles is close to the dipole vibrational energy of the Au nanocrystals, surface-plasmon resonance can occur, thereby improving the quantum efficiency due to the increase in the radiative recombination rates. In particular, the improved radiative recombination rates diminish the luminescence blinking, which normally deteriorates the quantum efficiency in nanoparticles. On the other hand, increasing the amount of Au causes the nanoparticles to become so close to each other that undesired nonradiative recombination becomes dominant, due to the destructive interference of the surface plasmons. Therefore, a decrease in luminescence is observed, as the excitons are delocalized by the thermal energy and, consequently, nonradiative recombination processes are activated.

The optimum Au fraction for the PL intensity is demonstrated in Fig. S3 (see Ref. 19) with the following assumptions: effective surface plasmons occur at a distance of between 10 and 70 nm from the Au surface, the surface-plasmon resonance increases the luminescence intensity by a factor of three, the CdS and Au nanoparticles are randomly distributed, and all of the overlapping interactions between the surface plasmons give rise to nonradiative recombination (shown as deep red in Fig. S3, see Ref. 19). The step-function approximation is a real simplification, while the actual enhancement factor is a complex function of the distance between CdS and Au (Refs. 30 and 31). However, the calculated quantum efficiencies based on this simple model are quite close to the experimental values, as shown in Fig. 3, and the experimental conditions are reflected quantitatively in Fig. S3 (see Ref. 19). For practical applications, this work can be applied to spectral converters in white light-emitting diodes through CdS/Au mixtures dispersed in an epoxy matrix.

In conclusion, to examine the influence of metal nanoparticles on the photoluminescence of semiconductors, colloidal mixtures of CdS and Au nanoparticles were prepared with different CdS/Au fractions. The existence of an optimum ratio of metal to semiconductor nanoparticles for the photoluminescence intensity indicates that interactions between the metal and semiconductor nanoparticles induced by surface-plasmon resonance occur constructively at appropriate distances.

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19See supplementary material at http://dx.doi.org/10.1063/1.3615782 for the XRD patterns, absorption spectra, and schematic figures of the colloidal Cds/Au nanoparticles.
Fig. S1. (Color) X-ray diffraction patterns of CdS and Au nanoparticles. The peak positions and intensities of CdS (JCPDS #75-0581) and Au (JCPDS #04-0784) are marked.
Fig. S2. (Color) (a) Absorbance, (b) absorptance, and (c) reflectance of mixed CdS/Au nanoparticles with various CdS/Au mole fractions.

\[ A + R + T = 1 \text{ (Absorptance} / \text{Reflectance} / \text{Transmittance)} \]
Fig. S3. (Color) Schematic figures of the distribution of the colloidal CdS/Au nanoparticles.
Fig. S4. Quantum efficiencies of the colloidal CdS nanoparticles as a function of the absorbance.
Table S1. The method for calculating the distance between Au nanoparticles.

By assuming that the Au nanoparticles (22 nm in diameter) have periodic FCC structure, the distances between Au nanoparticles are calculated (with $5.1 \times 10^{17}$ CdS nanoparticles/cm$^3$).

<table>
<thead>
<tr>
<th>CdS/Au Mole Fraction</th>
<th>10:0.5</th>
<th>10:1</th>
<th>10:2</th>
<th>10:4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance between Au Nanoparticles (nm)</td>
<td>234 nm</td>
<td>186 nm</td>
<td>148 nm</td>
<td>118 nm</td>
</tr>
<tr>
<td>Au Concentration (Au Nanoparticles/cm$^3$)</td>
<td>$1.1 \times 10^{14}$</td>
<td>$2.2 \times 10^{14}$</td>
<td>$4.4 \times 10^{14}$</td>
<td>$8.7 \times 10^{14}$</td>
</tr>
</tbody>
</table>