Understanding the Photothermal Conversion Efficiency of Gold Nanocrystals

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**Plasmon-based photothermal therapy** is one of the most intriguing applications of noble metal nanostructures. The photothermal conversion efficiency is an essential parameter in practically realizing this application. The effects of the plasmon resonance wavelength, particle volume, shell coating, and assembly on the photothermal conversion efficiencies of Au nanocrystals are systematically studied by directly measuring the temperature of Au nanocrystal solutions with a thermocouple and analyzing on the basis of energy balance. The temperature of Au nanocrystal solutions reaches the maximum at \( \sim 75 \, ^{\circ}C \) when the plasmon resonance wavelength of Au nanocrystals is equal to the illumination laser wavelength. For Au nanocrystals with similar shapes, the larger the nanocrystal, the smaller the photothermal conversion efficiency becomes. The photothermal conversion can also be controlled by shell coating and assembly through the change in the plasmon resonance energy of Au nanocrystals. Moreover, coating Au nanocrystals with semiconductor materials that have band gap energies smaller than the illumination laser energy can improve the photothermal conversion efficiency owing to the presence of an additional light absorption channel.

1. Introduction

Plasmonic Au nanostructures, such as nanospheres, nanorods, nanocages, and nanoshells, can absorb light and convert it to heat, which is thereafter transferred to the surrounding environment to cause a temperature increase. This photothermal conversion effect has been employed to selectively kill cancer cells,[1–7] controllably release gene[8,9] and deliver drugs,[10–12] image biological components on the basis of photothermal interference contrast,[13–15] optically record data five-dimensionally,[16] drive and guide liquid flow in microfluidic channels.[17] A critical factor for the successful use of plasmonic Au nanostructures in all of these applications is the photothermal conversion efficiency. Therefore, a thorough understanding of the effects of various experimental parameters on the photothermal conversion efficiency is very important. Several methods have been developed for the characterization of the photothermal conversion effect. The local temperature increases arising from the illumination of Au nanorods embedded in polymer matrices have been visualized with infrared cameras.[18] The photothermal conversion properties of Au nanospheres have been studied by embedding them in ice and measuring the time-dependent Raman signals of ice to monitor the melting process.[19] Thermochromic microcapsules have been utilized to reveal the temperature change by dispersing them together with Au nanospheres in liquids.[20] Moreover, coating Au nanocrystals with semiconductor materials has been found to improve the photothermal conversion efficiency owing to the presence of an additional light absorption channel.
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or complicated, and therefore difficult to be employed for simple and quick screening of the photothermal properties of a large number of noble metal nanostructures with varying sizes, plasmon wavelengths, and structure complexities.

Two recent experiments have demonstrated the continuous monitoring of the temperature variations of Au nanostructure dispersions under laser illumination by placing a thermocouple in the dispersions.\(^{[21,22]}\) In the first experiment, the temperature changes of SiO\(_2\)–Au core–shell, Au\(_2\)S–Au core–shell, and Au nanorod samples that have the same plasmon wavelength have been measured. The photothermal conversion efficiencies have been found to differ by a factor of 3 among the three Au nanostructure samples.\(^{[21]}\) In the second experiment, the photothermal properties of lithographically fabricated Au nanopyramids that have two different base diameters, two shell thicknesses, and two shapes have been determined. The Au nanopyramids with thin shells and sharp tips have been found to exhibit the largest photothermal response.\(^{[22]}\)

In this paper, we report on our systematic studies of the photothermal conversion properties of Au nanocrystals by placing a thermocouple in the aqueous Au nanocrystal dispersions to directly monitor the temperature rises under laser illumination. This direct measurement method is simple and easy to perform. The measurement in aqueous solutions is especially of a relevance to the biotechnological applications of noble metal nanostructures because the tissues and cells in biological systems are essentially in an aqueous environment. We have grown 20 Au nanorod (NR) samples that have longitudinal plasmon wavelengths ranging from 520 to 960 nm and 8 Au nanocrystal samples that have the same plasmon wavelength at 809 nm and measured their photothermal responses. The photothermal conversion efficiencies have been obtained from the modeling based on the energy balance and compared with those obtained from electrodynamic calculations. These measurements and modeling allow us to understand the effects of the plasmon wavelength and nanocrystal size on the photothermal conversion. Moreover, in many applications, metal nanostructures are required to be coated with different molecules and materials. Assembly and aggregation also occur when they interact with targeted objects. Both the shell coating and assembly can largely change the plasmonic properties of metal nanostructures. We have therefore further measured the photothermal responses of Au–ZnS and Au–Ag\(_2\)S core–shell nanostructures and studied the effect of the controlled assembly of one Au nanopolyhedron (NPH) sample and one Au NR sample on the photothermal conversion. The results and understanding arising from these studies will undoubtedly help in fully realizing the photothermal conversion-related applications of metal nanostructures.

2. Results and Discussion

2.1. Effect of the Plasmon Wavelength on the Photothermal Conversion

We first studied the effect of the plasmon wavelength on the photothermal conversion. Au NRs were chosen because NR samples with varying longitudinal plasmon wavelengths can readily be synthesized. The Au NR samples in our experiments were prepared using a seed-mediated growth method together with anisotropic shortening (see Supporting Information for the preparation details).\(^{[23,24]}\) The transmission electron microscopy (TEM) images of 6 representative NR samples are shown in Figure 1A–F, and their extinction spectra are shown in Figure 1G. The extinction spectra of all of the 20 NR samples are provided in Figure S1 in Supporting Information. Both the TEM images and extinction spectra indicate that these NR samples have narrow size distributions. The longitudinal plasmon wavelengths of the NR samples range from 520 to 960 nm, with an interval of ~20 nm per sample. Their lengths and diameters are in the ranges

Figure 1. Effect of the plasmon wavelength on the photothermal conversion. A–F) TEM images of the representative Au NR samples. Their average lengths/diameters are \((21 \pm 2)/(17 \pm 1), (29 \pm 2)/(17 \pm 1), (41 \pm 3)/(17 \pm 1), (43 \pm 3)/(13 \pm 1), (55 \pm 7)/(13 \pm 1), \) and \((64 \pm 6)/(12 \pm 1)\) nm from A) to F), respectively. G) Extinction spectra of the Au NR samples. The spectra from left to right are for the samples shown in A) to F), respectively. H) Experimental (symbols) and calculated (solid lines) temperature traces for the representative Au NR samples and pure water. The numbers indicate the longitudinal plasmon wavelengths of the NR samples. I) Dependence of the end temperature on the NR longitudinal plasmon wavelength. The end temperature is an average of the last 5 points for each trace.
of 20–65 and 10–20 nm, respectively. The extinction intensities at the longitudinal plasmon resonance peak wavelengths were adjusted to be around 2 for all of the NR samples for the photothermal measurements. The particle concentrations were estimated to be in the range of 0.3–1.5 nM. They decrease as the NR sizes become larger.

A simple home-designed setup (see Figure S2 in Supporting Information for the digital photo) was used for the photothermal conversion measurement. It was composed of a 1-cm path length quartz cuvette containing 2-mL of the Au NR solution, a thermocouple connected to a digital thermometer, and a continuous semiconductor diode laser (809 nm). The use of an 809-nm laser is because biological tissues have a window of high transmission in the spectral range of 650–900 nm.25 The measurement of the photothermal properties in this transmission window will be of important relevance to the biotechnological applications of metal nanostructures. The temperature was recorded every 30 s for 30 min after the laser was turned on. During the solution, the measurement was kept stirring with a small Teflon-coated magnetic stirring bar.

Figure 1H shows the temperature rise traces of the 6 representative NR samples under the laser illumination. The temperature traces of the other NR samples are provided in Figure S3 in Supporting Information. All of the traces exhibit a similar trend. The temperature first increases rapidly and then reaches a plateau after ~20 min. The end temperature varies with the longitudinal plasmon wavelength, as shown in Figure 1I. The end temperature for the Au NR sample with a longitudinal plasmon wavelength of 810 nm is 76 °C, which is the highest among all of the NR samples. If we consider the starting temperature of 21 °C, a remarkable maximum net temperature increase of 55 °C is obtained under our measurement conditions. For the NR samples with longitudinal plasmon wavelengths either shorter or longer than the illumination laser wavelength, the end temperature is lower. The variation of the end temperature versus the plasmon wavelength can be ascribed to the change in the extinction intensity at the laser wavelength. The extinction of noble metal nanostructures is contributed by both the absorption and scattering. Only the absorbed light energy can be converted into heat. For Au NRs, we have previously shown that the absorption-to-extinction ratio decreases nearly linearly with increasing diameters.24 The 20 NR samples employed in this experiment have two different diameters. Those with longitudinal plasmon wavelengths longer than 710 nm have an average diameter of 12 nm, while those with longitudinal plasmon wavelengths shorter than 710 nm have an average diameter of 17 nm. This is the reason for the presence of a jump around 710 nm in Figure 1H. When the plasmon resonance peak is shifted away from the laser wavelength, the extinction value and therefore the light absorption at the laser wavelength become smaller, leading to the reduction of the end temperature. In addition, the end temperatures achieved with the NR samples with longitudinal plasmon wavelengths between 760–860 nm range from 72–76 °C. The differences from the highest value are less than 5 °C. This result can be ascribed to the large widths of the longitudinal plasmon peaks of the NR samples. It allows us to choose Au NR samples with plasmon wavelengths over a certain range without being exactly equal to the illumination laser wavelengths in the applications involving the photothermal conversion.

We employed a theoretical model to analyze the photothermal conversion process and determine the photothermal conversion efficiency. The model is based on the energy balance of the Au NR solution during the photothermal heating process.20,26 Because the solution was kept stirring, the temperature is reasonably assumed to be uniform in the solution. The uniformity is also confirmed by measuring the temperatures at different positions in the solution after the steady state was reached under the laser illumination (Figure S4, Supporting Information). The energy balance can therefore be expressed as:

$$\frac{\Delta T}{\Delta t} = Q_{\text{loss}} - Q_{\text{laser}}$$  \hspace{1cm} (1)

where $m_1 = 2.00$ g is the mass of the solution, $c_{p,s} = 4.187$ J g$^{-1}$ K$^{-1}$ is the constant-pressure heat capacity of the solution, $m_c = 4.09$ g is the mass of the quartz cuvette, $c_{p,c} = 0.839$ J g$^{-1}$ K$^{-1}$ is the heat capacity of the quartz, $\Delta T$ is the difference between the solution temperature $T$ at time $t$ and the starting solution temperature $T_0$. $Q_{\text{laser}}$ is the energy arising from the laser illumination, and $Q_{\text{loss}}$ is the energy dissipated to the surrounding environment. There are two contributions for $Q_{\text{laser}}$. One is the light absorption by the Au NRs in the solution, and the other is the absorption by the cuvette walls and the solution. The second contribution is usually not included in common extinction spectra because of the use of references. It is small, but cannot be neglected, especially when the absorption by the Au NRs is very small. If the fraction of the laser energy absorbed by the cuvette walls and the solution is assumed to be $\zeta$, the two contributions to $Q_{\text{laser}}$ can then be written as:

$$Q_{\text{laser}} = I (1 - \zeta) \left(1 - 10^{-E_0}\right) \eta + I \zeta$$  \hspace{1cm} (2)

where $I = 1.72$ W is the reflection-corrected laser power that is incident on the system, $E_0$ is the extinction value at the illumination laser wavelength, and $\eta$ is the ratio of the absorption to extinction of the Au NRs. $\eta$ is also known as the photothermal conversion efficiency. The energy dissipation mainly occurs through the heat conduction and thermal radiation. It is usually expanded as a Taylor series of $\Delta T$. In our modeling, the first two terms are employed, which gives:

$$Q_{\text{loss}} = B \Delta T + C (\Delta T)^2$$  \hspace{1cm} (3)

where $B$ and $C$ are two coefficients. Combining Equation (1–3), we obtain:

$$\left(m_c c_{p,s} + m_s c_{p,c}\right) \frac{\Delta T}{\Delta t} = \left[I (1 - \zeta) \left(1 - 10^{-E_0}\right) + I \zeta \right] - B \Delta T - C (\Delta T)^2$$  \hspace{1cm} (4)

The unknown parameters $B$ and $C$ were determined by switching off the laser when the temperature rise reached the plateau. Under this condition, Equation (4) becomes...
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\[
(m_a c_p + m_c c_p,\text{d}) \frac{dT}{dt} = -B\Delta T - C (\Delta T)^2
\]  

(5)

By integrating \(\Delta T\) with respect to \(t\) and fitting the temperature decay curve (Figure S5, Supporting Information) with the obtained equation, we obtained \(B = 1.295 \text{ J} \cdot \text{K}^{-1} \cdot \text{min}^{-1}\) and \(C = 0.00803 \text{ J} \cdot \text{K}^{-2} \cdot \text{min}^{-1}\). \(C\) is much smaller than \(B\), justifying the above use of only two terms in Equation (3). \(\xi\) was determined by replacing the Au NR solution with water. In this case, Equation (4) becomes

\[
(m_a c_p + m_c c_p,\text{d}) \frac{dT}{dt} = I \xi - B\Delta T - C (\Delta T)^2
\]  

(6)

When the temperature rise reaches the steady state, the left side of Equation (6) becomes zero. In this way, \(\xi\) was determined from the end temperature (Figure 1H, Supporting Information) to be 0.0411.

After the parameters \(B\), \(C\), and \(\xi\) are known, the photothermal conversion efficiency \(\eta\) can then be determined by considering the steady state of the Au NR solution. At the steady state, the left side of Equation (4) becomes zero and the temperature reaches \(T_{\text{end}}\); \(\eta\) is therefore given by

\[
\eta = \frac{B(T_{\text{end}} - T_0) + C(T_{\text{end}} - T)^2 - I \xi}{I(1 - \xi)(1 - 10^{-\xi})}
\]  

(7)

In order to corroborate the validity of our theoretical model, we further solved Equation (4) and obtained the temperature as a function of time

\[
T = b \left[e^{\frac{9 - \text{al}}{a}} - 1\right] + T_0
\]  

(8)

where the parameters \(a\) and \(b\) are given by

\[
a = \frac{\xi}{2} + \sqrt{\frac{8\xi}{\pi} + \frac{4\xi}{2}}
\]  

(9)

\[
b = \frac{\xi}{2} - \sqrt{\frac{8\xi}{\pi} + \frac{4\xi}{2}}
\]  

(10)

\[
D = \frac{1}{2}(1 - \xi)(1 - 10^{-\xi}) \eta + I \xi
\]  

(11)

Equation (8) was employed to model the photothermal conversion process of the Au NR samples with different plasmon wavelengths. The calculated temperatures are plotted as solid lines in Figure 1H and Figure S3 in Supporting Information. No fitting parameters were used in the calculation. The obtained temperature rise traces agree remarkably well with the experimental ones, suggesting that the model is very robust and reliable and that there are no temperature gradients in the solutions. It was therefore utilized to analyze the photothermal conversion process in the following studies of the effects of the particle volume, shell coating, and assembly on the photothermal conversion.

2.2. Effect of the Particle Volume on the Photothermal Conversion

For the study of the particle volume effect, we prepared 3 Au NR samples and 5 Au nanobipyramid (NBP) samples by combining the seed-mediated growth together with the anisotropic shortening and transverse overgrowth,\[23,24,27,28\] the synthesis details are provided in Supporting Information. Because the end temperature has been found above to be the highest when the plasmon wavelength of Au nanocrystals is equal to the illumination laser wavelength, the longitudinal plasmon wavelengths of the 8 samples were all synthetically controlled to be 809 nm. Figure 2A–H show the TEM images of the Au nanocrystals in the order of increasing particle volumes. For the purpose of better comparison, only one nanocrystal is shown per image, and they are all shown at the same magnification and aligned horizontally. The TEM images of the ensemble nanocrystal samples are given in Figure S6 in

![Image](https://example.com/image.png)
Supporting Information. The Au NRs have a cylindrical shape with smooth surfaces, while the Au NBPs are composed of two pentagonal pyramids with a common base in the middle and the two pyramids pointing to the opposite directions. All of the 3 NR samples and the first 3 NBP samples have smooth surfaces, while the surfaces of the last 2 NBP samples are rough. These nanocrystal samples possess narrow size distributions. Their average sizes and volumes, together with their given names, are listed in Table 1. The difference in the particle volume between the largest and smallest nanocrystal sample amounts to 200 times.

The extinction intensities of the 8 Au nanocrystal samples at their longitudinal plasmon resonance peaks were adjusted to be around 2 (Figure 2I, left side) for the photothermal conversion measurements. The particle concentrations were estimated to be in the range of 0.005–1.0 nM. The temperature rise traces are shown in Figure S7 in Supporting Information. The end temperatures obtained from these traces are given in Table 1. Even though the Au nanocrystal samples have the same extinction value at the illumination laser wavelength, the end temperatures reached after the illumination for 30 min vary considerably. The end temperature is found to increase with decreasing particle volumes. The end temperature of the smallest NRs is the highest, amounting to 77 °C, while the largest NBPs exhibit the lowest end temperature of 55 °C.

The variation in the end temperature should arise from the difference in the photothermal conversion efficiency among the Au nanocrystal samples, because their extinction values at the illumination wavelength are the same. The photothermal conversion processes of the 8 Au nanocrystal samples were therefore modeled to determine their photothermal conversion efficiencies. Excellent agreements between the experimental and calculated temperature traces are obtained (Figure S7, Supporting Information). The photothermal conversion efficiencies are plotted in Figure 2J. They range from 13% to 96% and decrease as the effective radius is increased. This overall trend is consistent with that obtained from the experiments. When the effective radius is below ~15 nm, the calculated efficiencies are very close to the measured ones. However, when the effective radius is above ~15 nm, the calculated efficiencies are smaller than the measured ones, and the difference becomes larger as the effective radius is increased. We believe that this observed difference between the experiments and calculations can be ascribed to the re-absorption of the scattered light by the nanocrystals in the solution. This factor causes the measured conversion efficiency to be larger than the calculated one. As the sizes of the nanocrystals get larger, the re-absorption of the scattered light contributes more to the entire photothermal conversion, because the contribution of the scattering to the extinction increases rapidly with increasing nanocrystal sizes. Our study of the effect of the particle volume highlights again the powerfulness of our measurement method in understanding the fundamental aspects of the photothermal conversion efficiency and rapidly screening metal nanostructures with desired conversion efficiencies. In addition, it will also be interesting to explore the nanocrystal shape on the conversion efficiency, which is currently limited by the capability to prepare metal nanocrystals of different shapes but the same particle volume.

Table 1. End temperatures of the Au nanocrystals with the same longitudinal plasmon wavelengths and different volumes.

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<tr>
<td>Largest NBPs</td>
<td>173 (16)</td>
<td>77 (7)</td>
<td>537100</td>
<td>55.4</td>
</tr>
<tr>
<td>Larger NBPs</td>
<td>137 (11)</td>
<td>50 (4)</td>
<td>132000</td>
<td>68.4</td>
</tr>
<tr>
<td>Medium NBPs</td>
<td>125 (9)</td>
<td>39 (2)</td>
<td>62800</td>
<td>71.9</td>
</tr>
<tr>
<td>Smaller NBPs</td>
<td>85 (12)</td>
<td>32 (2)</td>
<td>32400</td>
<td>74.0</td>
</tr>
<tr>
<td>Smallest NBPs</td>
<td>74 (8)</td>
<td>24 (2)</td>
<td>13400</td>
<td>74.3</td>
</tr>
<tr>
<td>Large NRs</td>
<td>63 (7)</td>
<td>15 (3)</td>
<td>10300</td>
<td>75.3</td>
</tr>
<tr>
<td>Medium NRs</td>
<td>55 (7)</td>
<td>13 (1)</td>
<td>6700</td>
<td>75.6</td>
</tr>
<tr>
<td>Small NRs</td>
<td>38 (5)</td>
<td>10 (2)</td>
<td>2700</td>
<td>77.0</td>
</tr>
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</table>

a) The numbers in the parentheses are standard deviations. b) The diameters of the NBPs were measured at the middle.
2.3. Effect of the Shell Coating on the Photothermal Conversion

We next studied the effect of the shell coating on the photothermal conversion efficiency, because the plasmon wavelengths of metal nanostructures have been well known to be highly sensitive to the dielectric properties of the surrounding medium. Moreover, the surrounding dielectric layer can be made of semiconductors with appropriate band gaps to enhance the overall light absorption. On the basis of these considerations, we prepared two Au nanocrystal–semiconductor core–shell nanostructures and measured their photothermal properties. The cores are Au nanopolyhedrons (NPHs) and the shells are either ZnS or Ag$_2$S. Their preparation followed our reported procedure,\cite{30} with the details provided in Supporting Information. Figure 3 A shows the scanning electron microscopy (SEM) image of the uncoated Au NPH sample. It has an average diameter of (43 ± 1) nm. When dispersed in aqueous solutions, it has a plasmon wavelength of 545 nm (Figure 3D). Figure 3 B and C show the TEM images of the NPH–ZnS and NPH–Ag$_2$S core–shell nanostructures, respectively. The ZnS shell is porous, while the Ag$_2$S shell is dense. The refractive index of ZnS is –2, and that of Ag$_2$S is in the range of 2.5–3.5 in the near infrared spectral region.\cite{31, 32} The shell coating results in large red shifts in the plasmon resonance peak. The plasmon wavelengths of both core–shell nanostructures were controlled to be 770 nm by varying the shell thicknesses during the synthesis.\cite{30} As a result, the overall average diameters of the NPH–ZnS and NPH–Ag$_2$S nanostructures are (160 ± 8) and (88 ± 8) nm, respectively. The control of the two types of nanostructures to have the same plasmon wavelength ensures that the effect of the plasmon wavelength on the photothermal conversion efficiency is the same. The extinction intensities at the plasmon resonance peaks were all adjusted to be ~2 for the uncoated Au NPH sample and the two nanostructure samples (Figure 3D).

The temperature rise traces for the three samples are compared in Figure 3E. Because the extinction intensity of the uncoated Au NPH sample at 809 nm is 0.06, which is very small, the end temperature resulting from the photothermal conversion is only 25 °C. In contrast, the extinction intensities at 809 nm are 1.7 for both of the core–shell nanostructure samples. The measured end temperatures for the NPH–ZnS and NPH–Ag$_2$S samples are 60 and 71 °C, respectively. The photothermal conversion processes of the three samples were then analyzed, as shown by the solid curves in Figure 3E, and the obtained conversion efficiencies are 18%, 64%, and 86%, respectively. This result indicates that the photothermal conversion efficiencies of metal nanocrystals can be increased by shifting their plasmon resonances towards the illumination laser wavelength through shell coating. Moreover, even though the extinction intensities at 809 nm are the same for the two nanostructure samples, the conversion efficiency of the NPH–Ag$_2$S sample is 1.4 times that of the NPH–ZnS sample. The difference in the conversion efficiency is ascribed to the different light absorption behaviors of the Ag$_2$S and ZnS shells at 809 nm. Ag$_2$S and ZnS are semiconductors. Their band gaps have previously been measured to be 0.9–1.1 and 3.4–3.8 eV, respectively.\cite{31, 32} The former is smaller, while the latter one is larger than the illumination photon energy. Therefore, the ZnS shell is transparent to the illumination laser, while the Ag$_2$S shell can strongly absorb it. The additional light absorption introduced by the Ag$_2$S shell causes the conversion efficiency of the Au NPH–Ag$_2$S sample to be higher than that of the NPH–ZnS sample. This result suggests that coating metal nanocrystals with strongly light-absorbing materials can increase the photothermal conversion efficiencies.

2.4. Effect of the Assembly on the Photothermal Conversion

We finally studied the effects of the assembly of metal nanocrystals on the photothermal conversion efficiency. Such studies are highly relevant to the photothermal killing of cancer cells with metal nanocrystals, because typically a number of metal nanocrystals are aggregated on cancer cells during photothermal therapy.\cite{1–7} Two cases were considered. In the first case, the plasmon resonance wavelength of spatially isolated metal nanocrystals is far away from the illumination laser wavelength, where the extinction intensity is nearly zero. After the assembly, the extinction intensity at the illumination wavelength is greatly increased. The assembly induces a large red shift of the plasmon resonance peak, which causes a great reduction in the extinction intensity at the illumination wavelength. The Au NPH sample and one of the NR samples were chosen. Their assembly was realized by the addition of 0.01 M glutathione in the solutions. The growth of the two nanocrystal samples and their assembly followed our reported procedures,\cite{23, 24, 33–35} and the details are provided in Supporting Information.

Figure 4A shows the time-dependent extinction spectra of the NPH solution recorded after the addition of glutathione.

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**Figure 3.** Effect of the shell coating on the photothermal conversion. A) SEM image of the Au NPH sample. B) TEM image of the core–shell Au NPH–ZnS nanostructures. C) TEM image of the core–shell Au NPH–Ag$_2$S nanostructures. D) Extinction spectra of the three samples shown in A–C. The particle concentration of the Au NPH sample is estimated to be 0.24 nM. E) Experimental (symbols) and calculated (solid lines) temperature traces for the three samples.
The plasmon wavelength of the isolated Au NPH sample is 545 nm. The addition of glutathione induces the assembly of the NPHs. The plasmon resonance peak corresponding to the isolated NPHs decreases in intensity. At the same time, a broad peak appears in the spectral region of 700–1100 nm. The occurrence of this broad peak causes a large increase in the extinction intensity at 809 nm. The assembly of the NPHs is corroborated by the TEM imaging. The NPHs are randomly distributed in the absence of glutathione (Figure 4B). They are assembled into chains in the presence of glutathione (Figure 4C). The effect of the assembly on the photothermal conversion is revealed by the temperature trace shown in Figure 4D, where the extinction intensity of the starting NPH sample at its plasmon resonance peak wavelength was adjusted to be around 2. The resultant particle concentration is estimated to be ∼0.2 nM. At the starting stage of the laser illumination, the temperature rise trace of the NPH solution appears similar to that indicated with the black circles in Figure 3E. The quick injection of 20 μL of the glutathione solution at 30 min triggers a rapid temperature increase from 25 to 43 °C within ~10 min. This rapid temperature rise is caused by the increase in the extinction intensity at 809 nm owing to the assembly of the Au NPHs in the solution. Because the added volume of the glutathione solution is very small, the temperature drop at 30 min is unobservable. After reaching the maximum of 43 °C, the solution temperature starts to decrease steadily and stabilizes finally at 30 °C. The temperature decrease can be explained by looking at the extinction spectra shown in Figure 4A for the assembly. The extinction intensity at 809 nm reaches the maximum at ~8 min after the addition of glutathione. The time period is approximately the same as that taken for the NPH solution to arrive at its maximum temperature. After reaching the maximum, the extinction intensity at 809 nm starts to decrease because the plasmon peak red shifts as more NPHs are assembled together. The absorption of less light power induces the reduction in the solution temperature.

The Au NR sample with a longitudinal plasmon wavelength of 810 nm was used for the second situation. The extinction intensity at its longitudinal plasmon peak was adjusted to be around 2.0. The resultant particle concentration was estimated to be ∼0.4 nM. The addition of glutathione induces a reduction in the extinction intensity at the longitudinal plasmon peak and a concomitant appearance of a new peak in the longer-wavelength region (Figure 4E). The glutathione-induced assembly of the Au NRs is corroborated by the TEM imaging. In the absence of glutathione, the NRs are randomly distributed (Figure 4F). They are aligned into chains in the presence of glutathione (Figure 4G). The temperature of the NR solution rises to 77 °C after 30 min of the laser illumination (Figure 4H). It shows a gradual decrease after the addition of glutathione and finally becomes stabilized. This temperature drop can clearly be ascribed to the assembly-induced decrease in the extinction intensity at the illumination laser wavelength. The results obtained from the two assembly situations indicate that the assembly state of metal nanocrystals has a strong effect on the plasmon-based photothermal conversion. This effect should be fully taken into account for the development of highly efficient, plasmon-based phototherapy agents. In addition, target-selective...
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phototherapy agents might be developed if the assembly process of metal nanocrystals can be designed to be triggered by the presence of some specific biological species.

3. Conclusions

The photothermal conversion efficiencies of Au nanocrystals have been found to be strongly dependent on the plasmon resonance wavelength, nanocrystal volume, shell coating, and assembly state. Au nanocrystal solutions reach the highest temperature when the plasmon resonance wavelength is equal to the illumination laser wavelength. The photothermal conversion efficiency decreases as the particle volume of Au nanocrystals that are similarly shaped gets larger, because the fraction of the excitation light power that is scattered becomes larger. Coating of Au nanocrystals with appropriate materials can improve the plasmon-based photothermal conversion through two effects. One is the shift in the plasmon resonance wavelength arising from the change in the refractive index of the surrounding medium, and the other is the increase in light absorption resulting from the use of semiconductor coating materials with suitable band gap energies. Moreover, assembly of Au nanocrystals has been found to be an effective means for controlling their photothermal conversion properties. Our results are useful not only for understanding the fundamental aspects of plasmon-based photothermal conversion but also for designing metal nanostructure-based phototherapy agents with improved efficiencies and flexibilities.

4. Experimental Section

Characterization: The SEM imaging was performed using an FEI Quanta 400 FEG microscope. The TEM imaging was performed on a Philips CM120 microscope operating at 120 kV. The setup for the measurement of the photothermal conversion was composed of a 1-cm path length quartz cuvette that was covered with a foam cap, a K-type thermocouple connected to a digital thermometer (CIE 305), and a continuous semiconductor diode laser (809 nm, JUM2500/50/20, VDM00036, JENOPTIK, Germany). The laser power was measured with a laser power meter. In order to reduce the heat loss, the cuvette was clamped at its top part above the probe head of the thermometer. The bottom of the cuvette was kept ∼5 cm above the magnetic stirrer. The laser light was coupled out through an optical fiber and illuminated on the Au NR solution in the cuvette with a spot diameter of ∼5 mm. The probe head of the thermocouple was completely submerged in the solution and carefully kept away from the direction illumination by the laser light.

FDTD calculation: The FDTD calculations were performed using a commercial software, FDTD Solutions 6.0 (Lumerical Solutions). The Au dielectric function was formulated according to the Drude model with the parameters chosen to match the experimentally measured dielectric data. The Au nanocrystal and its surrounding medium were divided into meshes of 0.5 nm in size. The excitation electric field was set to be polarized along the length axis of the nanocrystal. The surrounding medium was taken as water with a refractive index of 1.333. The sizes and shapes of the Au nanocrystals were set to be as close as possible to those measured from the TEM images. Specifically, the NR was modeled as a cylinder capped with a hemisphere at each end. The NPB was modeled as two pentagonal pyramids with their two apexes truncated spherically.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

Acknowledgements

Support from NSFC (Project Code: 20828001), CUHK Block Grant (Project Code: 3110046), and RGC GRF (Ref. No.: CUHK403409, Project Code: 2160391) is greatly acknowledged.


Received: June 30, 2010
Published online: September 8, 2010