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Gold Nanorods: Near-Infrared Plasmonic Photothermal Conversion and Surface Coating

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ABSTRACT

In this paper, AuNRs colloids with SPR_L located at ~810 nm and ~1100 nm were synthesized using an improved seed method. Based on the NIR lasers available, photothermal conversion of AuNRs were systematically studied compared with that of water. Under low power irradiation, the highest temperature is obtained when the SPR_L wavelength of AuNRs is equal to the laser wavelength, and temperature of colloid increases from ~20˚C to ~65˚C. With increasing laser power (such as 6 W), the AuNRs colloid boils within a few minutes, and nanorods undergo a shape deformation from rod to spherical particle and even fusion, and the SPR_L disappears. For further investigation, the obtained AuNRs were coated with SiO_2 shell to form a core-shell nanostructure (Au@SiO_2). The surface coating can be used not only in keeping the stability of AuNRs for further treatment, but also in increasing plasmonic property and biocompatibility. This work will be useful for designing plasmonic photothermal properties and further applications in nanomedicine.

KEYWORDS

Gold Nanorods; Surface Plasmon Resonance; Photothermal Effect; Core-Shell

1. Introduction

Gold nanorod is one of the most studied colloidal nanostructures for its two distinct surface plasma resonances (SPR), known as the transverse mode (SPR_T) and longitudinal mode (SPR_L) [1-4]. The SPR_T is weak and located at ~520 nm, while the strong SPR_L can be tuned in the visible-near infrared (Vis-NIR) region [5-7]. Wet chemical fabrication of AuNRs was pioneered by Murphy and coworkers through a citrate-capped seed technique [8,9]. Improvement of this method for producing AuNRs with high yield was achieved by introduction of CTAB [10-12].

The optical tunability of AuNRs has brought several advantages to AuNRs. For example, using the tunability (and sensitivity) of SPR to aspect ratios of AuNRs and polarization of light, five-dimensional optical recording-reading process was realized [13]. The changes of density of surface charge and surrounding index can be used for the direct observation of chemical reactions [14,15]. The high dependence of SPR_L on aspect ratios, surface coating, and aggregation degree or assembly is promising for chemical and biological sensing. The NIR SPR_L extinction is consistent with the human tissue facilitating photothermal therapy and solar energy harvesting [16-19]. For *in-vivo* therapy in cancer research, small diameter AuNRs are more ideal metal nanostructures for cancer diagnosis and therapy for their tunable SPR_L and optimal penetration through biological skin and tissue in the NIR region [20-25]. And the photothermal conversion efficiency is an essential parameter in the therapy [26,27].

However, due to the toxicity of CTAB covered on AuNRs, surface coupling with biological compatibility molecular was usually proposed for application research [28]. On the other hand, surface coating with medium to form a core-shell structure also provides an effective way to keep the stability in further treatment. Silica (SiO_2), as a gain medium for plasmonic property and advantage of biological compatibility and chemical stability, was a promising coating medium, especially for surface coating of AuNRs [29]. The SiO_2 coating can be used not only in keeping the stability of AuNRs for further treatment, but also in increasing plasmonic property and biocompatibility.

In this work, AuNRs colloids with SPR_L absorption peaks were synthesized using an improved "seed" method. Based on the NIR lasers available, such as 808

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nm and 1064 nm, the photothermal conversion of AuNRs colloids was studied under different irradiation performance. [30] Under laser radiation, temperatures of AuNRs colloids rise obviously. With increasing the laser power (such as 6 W), the AuNRs colloid boils within a few minutes, and nanorods undergo a shape deformation from rod to spherical particle and even fusion. For further research, SiO_2 coating on AuNRs to form Au@SiO_2 core-shell structure was also carried out.

2. Experiment Section

2.1. Synthesis of AuNRs

AuNRs colloids with desired SPR_L wavelengths (such as 810 nm and 1100 nm) can readily be synthesized through a similar process, as reported previously [31,32]. Briefly, in the first step, the seed solution for AuNRs was prepared by dissolving $HAuCl_4$ (0.05 mL, 0.05 M) in an aqueous solution of CTAB (10 mL, 0.1 M). Then, ice-cold $NaBH_4$ (0.6 mL, 0.01 M) was injected into the solution under vigorous stirring. In the second step of the growth solution for GNRs with SPR_L at 805 nm, 0.912 g CTAB together with 0.110 g 5-bromosalicylic acid was dissolved in 49 mL water. Then $AgNO_3$ (0.24 mL - 1 mL, 0.02 M) was added under stirring, followed by addition of $HAuCl_4$ (0.5 mL, 0.05 M). Then 0.13 mL (0.1 M) AA solution was added with stirring until the solution became colorless. After aging 30 min, 0.06 mL "seed" solution was added into the as-prepared growth solution, and AuNRs can be obtained after 12 h.

2.2. Photothermal Conversion of AuNRs

The setup for the measuring the photothermal conversion was composed of a 10 mm path length quartz cuvette, a sensitive digital thermometer (TM-902C), and continuous lasers (including 808 nm laser coupled out through an optical fiber, GKFCM-808; semiconductor diode 980 nm laser; and 1064 nm, GKNQL-1064). The laser power was obtained from the P-I curves. The laser light illuminated on the AuNRs colloid in the cuvette. After each irradiation, the probe head of the thermocouple was completely submerged in the colloid immediately. The temperature of the colloid is reasonably assumed to be uniform in the solution for the same testing data at different positions.

2.3. Surface Silica Coating AuNRs

0.04 mL NaOH (0.1 M) solution was added into the as-obtained Au NRs colloid (4 mL) with a certain CTAB concentration under stirring. Then 0.04 mL TEOS (in ethanol) was injected into Au NRs colloid under gentle rotary shaking for the hydrolysis of TEOS and SiO_2 coating on the surface of Au NRs. Au@SiO_2 core-shell structure was obtained after 20 h.

2.4. Characterization

UV-Vis-NIR spectra of prepared solution were collected by spectrophotometer (UV-6300) in the wavelength range of 200 - 1100 nm. The products were purified by first centrifugating at 3000 RPM for 20 min to remove the large sized particles deposited on the bottom of centrifugal tube. Then the colloids were centrifugated repeatedly at 14000 RPM with deionized water. Then the samples were deposited on copper grids covered by an amorphous carbon film for transmission electron microscope (TEM: JEOL-100CX) measurements.

3. Results and Discussion

The microstructure and growth mechanism of the AuNRs were studied in detail, as reported previously [31]. Fig. 1a shows the normalized UV-Vis-NIR absorption spectra for the AuNRs colloids. In addition to the strong and tunable SPR_L absorption peak located at ~810 and 1100 nm, respectively, there is a weak resonance peak located at ~520 nm, originated from the SPR_T absorption of nanorods and possible existence of spherical nanoparticles and nanocubes. TEM images of the AuNRs with SPR_L located at ~810 nm, and ~1100 nm are shown in **Figures 1(b)** and **(c)**. The sizes of the AuNRs are nearly uniform.

The effects of the SPR wavelength and NIR laser on the photothermal conversion efficiencies of AuNRs are studied by measuring the temperature increase, compared with that of water. Under low power irradiation, it is shown that the highest temperature is obtained when the SPR_L wavelength of AuNRs is equal to the illumination laser wavelength, and temperature of the colloid rises from ~20˚C to ~65˚C, which is accordant with the reported work [32]. However, the photothermal efficiency

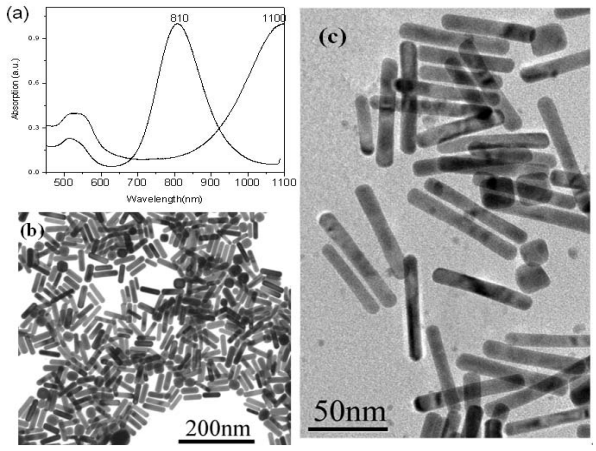

Figure 1. UV-Vis-NIR absorption spectra (a) and TEM images for the as-prepared AuNRs colloids with SPR_L absorption located at ~810 (b) and ~1100 nm (c).

decreased with increasing irradiating time. As shown in **Tables 1** and **2** for the photothermal effect of AuNRs colloid (1 mL) with SPR_L peaks located at ~805 and 1100 nm irradiated, respectively, under 808 and 1064 nm lasers. Since AuNRs were dispersed in deionized water, we used the heat capacity of water 4.2 J/g in calculating the efficiency of AuNRs colloid.

Figures 2(a) and **(b)** showed the optical absorption spectra of AuNRs colloids before and after irradiation with high laser power. After the AuNRs colloid with SPR_L at 810 nm was irradiated under 808 nm laser (6 W) for 3 min, the intensity of SPR_L decreased sharply, and the absorption damped over the whole region. The SPR_L at 1100 nm disappeared after the AuNRs colloid was irradiated by 1064 nm laser (7 W) for 8 min, and only the absorption peak of gold spherical nanoparticles was observed, as inserted one in **Figure 2(b)**.

With increasing the laser power (such as 6W for 808 nm laser), the AuNRs colloid would boil within a few minutes. After the strong irradiation, the color of the colloid faded with products deposited on the bottom. Corresponding to the optical spectra changes of the AuNRs colloid under strong laser irradiation, TEM images indicated that nanorods undergo deformation from rod to spherical particle and even fusion under irradiation of high power. **Figures 3(a)**, **(b)** presents the TEM images of the AuNRs (with SPR_L at 1100 nm) before and after laser irradiations. After the AuNRs colloid was irradiated with 1064 nm laser (7 W) for 8 min, the aspect ratio decreased and large sized nanoparticles were observed. The morphology evolution of the AuNRs under high power laser irradiation can be used to explain the disappearance of SPR_L and the photothermal efficiency decrease of AuNRs colloid with increasing irradiating time.

Table 1. Photo-thermal effect of AuNRs colloid (1 mL) with SPR_L peaks located at ~810 nm under 808 nm lasers (laser spot size: 2 mm) irradiation. (In calculating the efficiency of AuNRs colloid, the heat capacity of water is 4.2 J/g).

Power (W)	Irradiation time (min)	T(˚C) of sample before and after irradiation	Efficiency of AuNRs colloid	T(˚C) of pure water before and after irradiation	Efficiency of pure water
	2	22/27	0.525	18/18	0
0.333	5	22/31	0.372	18/18	0
	10	22/35	0.269	18/19	0.021
	2	22/35	0.682	19/20	0.0525
0.667	5	22/46	0.503	19/22	0.063
	10	22/52	0.315	19/23	0.042
	2	22/36	0.612	20/21	0.0438
0.800	5	22/48	0.455	20/24	0.07
	10	22/57	0.30625	20/27	0.0613

Table 2. Photo-thermal effect of AuNRs colloid (1 mL) with SPR_L peaks located at 1100 nm under 1064 nm lasers (laser spot size:r = 1 mm) irradiation.

Power (W)	Irradiation time (min)	T(˚C) of sample before and after irradiation	Efficiency of AuNRs colloid	T(˚C) of water before and after irradiation
	2	23/29	0.2625	23/24
0.8	5	23/36	0.2275	23/25
	10	23/41	0.1575	23/26
	2	23/38	0.4375	22/23
1.2006	5	23/46	0.268	22/25
	10	23/53	0.175	22/27
	2	23/42	0.407	23/25
1.6328	5	23/53	0.257	23/27
	10	23/63	0.171	23/30
7	2	22/74	0.52	

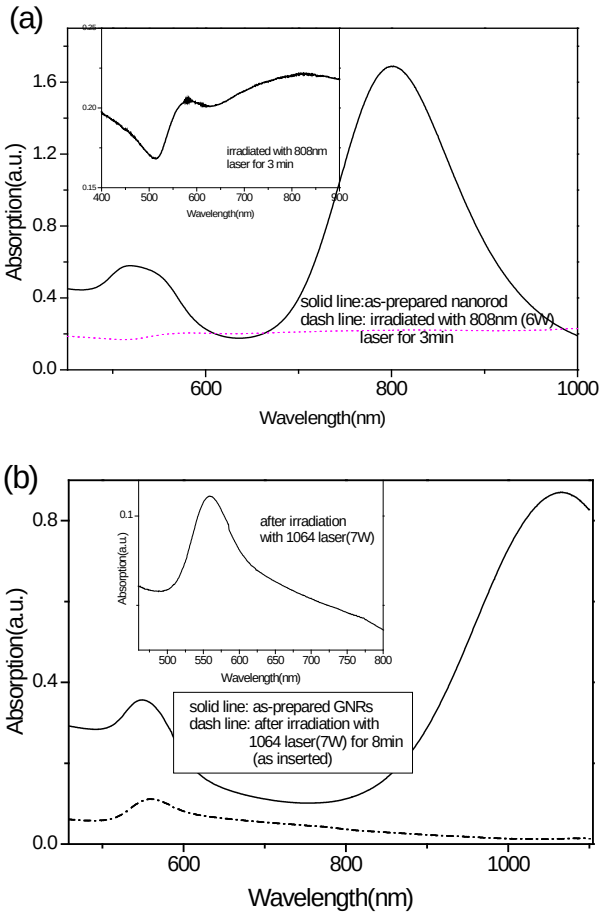

Figure 2. UV-Vis-NIR absorption spectra of AuNRs colloids before and after irradiation with high laser power, insets are the spectra of AuNRs after irradiation. AuNRs colloids with SPRL located at ~810 nm (a) and 1100 nm (b) before and after irradiation under 808 nm laser (6 W, 3 min) and 1064 nm laser (7 W, 2 min), respectively.

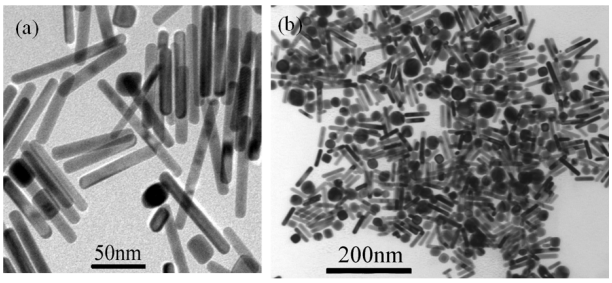

Figure 3. (a), (b) TEM images of the AuNRs (with SPRL at 1100 nm) before and after irradiations under 1064 nm laser (7 W) for 8 min.

Figure 4(a) presents the TEM image of AuNRs after SiO_2 coating. It can be seen that most of the AuNRs, together with some Au nanoparticles, have been successfully sealed by homogeneous SiO_2, and formed core-shell $Au@SiO_2$ nanostructure. Also, there are a few SiO_2 nanospheres without AuNRs core. By controlling the

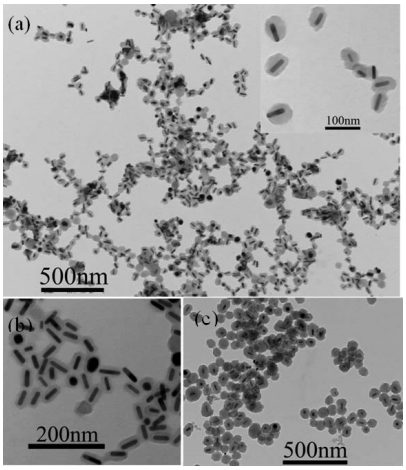

Figure 4. (a)TEM images of silica-coated AuNRs. Insertion of (a) is the magnified image of core-shell structured $Au@SiO_2$. (b-c) TEM images of AuNRs coated with silica shells of different thickness.

coating time, volume of TEOS/ethanol, and the concentration of AuNRs, we were able to vary the shell thickness (**Figures 4(b)** and **(c)**). In the experiment, it is found that certain CTAB coverage on the surface of AuNRs is very important for the SiO_2 capping. And further experiments are now being carried out.

4. Conclusion

In summary, we have demonstrated the synthesis of AuNRs with SPR_L in the NIR region. The photothermal conversion efficiencies of AuNRs were studied. An obvious temperature increasing was observed in the photothermal conversions of AuNRs under laser irradiation. The highest temperature is obtained when the SPR_L wavelength of AuNRs is equal to the laser wavelength, and temperature of the colloid increased up to ~65 ˚C even at low irradiating power. At a relative high power (such as 6 W), nanorods undergo deformation from rod to spherical particle and even fusion $Au@SiO_2$ core-shell structure was obtained, and further comparing experiments, such as photothermal conversions and stability are now being carried out.

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