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Fabrication and near-infrared photothermal conversion characteristics of Au nanoshells

Zhongxin Liu, Hongwei Song,[a] Lixin Yu, and Linmei Yang
Key Laboratory of Excited State Physics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 Eastern Nan-Hu Road, Changchun 130033, People's Republic of China

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In this letter, gold nanoshells with a size of ~20 nm were prepared by a wet-chemical synthesis method and the surface plasmon absorption band of gold was tuned from visible to near-infrared. The gold nanoshell hydrosol demonstrated excellent photothermal conversion property. The temperature of the hydrosol was increased to as high as 30 °C under exposure of an 808 nm coherent diode laser with a powder density of 5 W/cm^2. This kind of gold nanoshell hydrosol is promising for use in biomedicine through photothermal conversion. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1874308]

Noble metal nanostructures have been the focus of study for many decades because of their use in real or potential applications, such as catalysis, photography, optics, electronics, optoelectronics, information storage, biological and chemical sensing, and surface-enhanced Raman scattering (SERS).[1–3] It has been demonstrated that the intrinsic properties of a metal nanostructure are closely related to the shape, size, and structure. The nanometer noble metals with various kinds of shape have been prepared, such as nanospheres,[1] nanorods,[4] nanobelts,[5] nanodisks,[6] nanoprism,[7] nanotubes, nanoshells, nanoboxes,[8] and nanocapsules, and their intrinsic properties were widely studied. Among them, colloidal hollow gold (nanoshells) have been studied extensively in recent years due to their special optical properties and promising applications in biomedicine.[9] The strong surface plasmon absorption band for gold nanoshells can be tuned from visible to the near-infrared (NIR) region of 800–1200 nm, where the transparent window of biological tissues is located.[10] Using moderately low exposures of extra corporeally applied NIR light, the nanoshells injected into the tissues of a body can be used to deliver a therapeutic dose of heat to kill the sick cells. Thus, gold nanoshells have become an ideal candidate for photothermally trigged drug releasing in tissues. In 2003, Halas *et al.*[11] reported the application of gold shells packed on SiO_2 nanoparticles (100 nm) to thermal ablative therapy for cancer. Later, Sun *et al.*[1,2] reported the preparation of hollow gold nanoshells with a size of ~50 nm and their NIR absorption properties. In their preparation, poly (vinyl pyrrolidone) was used as a capping reagent and a high preparation temperature was required. Here, we present an easier way to synthesis Au nanoshells with a size of ~20 nm along with their excellent photothermal conversion properties. The shells with a smaller size should have better stability in solutions and a better metabolic property in the body.

First, spherical silver particles were prepared by the conventional method.[12] In the preparation, 0.25 mL $AgNO_3$ (0.1 mM, Aldrich) was added to 100 ml deionized water and 0.25 mL citrate (0.2 M) was added in the mixture and stirred for 10 min. Then, 1 ml of fresh $NaBH_4$ (0.01 mM) was injected. The color of the solution changed to dark yellow immediately. Then, the solution was stirred for 30 min until the color was stable. After that, 20 ml above solution was heated at 100 °C in a 250 ml flask and refluxed for 10 min before a specific volume of 1 mM $HAuCl_4$ (99.9%, Aldrich) aqueous solution was added dropwise. The color of the solution turned from yellow to green and then gradually blue. The reaction mixture was refluxed for another 20 min until its color became stable. Vigorous magnetic stirring was maintained in the entire process. The products were cooled to room temperature and deposited for at least 6 h before measurements.

The absorption spectra were measured with a Shimadzu UV-3101PC ultraviolet visible (UV-VIS) NIR scanning spectrophotometer. The morphology and size of the particles were observed with a JEM-2010 transmission electron microscope (TEM) (JEOL Company, Japan). In the photothermal conversion experiments, different volumes of gold nanoshell hydrosol with an absorption peak of ~800 nm (Sample d in Fig. 2) were diluted to 2 mL by distilled water in a culture dish (with a cross section of 2 cm^2 and height of 1.8 cm). The solutions were exposed to a B-TEC-30-01 electrically cooled coherent 808 nm fiber-coupled diode laser (made by Changchun Institute of Optics, Fine Mechanics and Physics, CAS) with an irradiation area of 2 cm^2 and power of 10 W. The temperature of the solution was detected with the NRL-002 sensitive thermal detector (made by Changchun Maida Co., Ltd. of China). The experimental equipment was drawn in Fig. 1.

Figure 2 shows the absorption spectra of silver nanospheres before and after a reaction with different volumes of $HAuCl_4$ solution. As seen, the silver nanoparticles exhibited an intense and characteristic surface plasmon absorption peak at 400 nm. As a small volume (0.3 mL) of $HAuCl_4$ solution was added, the intensity of the 400 nm band decreased, while two bands at 450 and 700 nm appeared. With the increase of $HAuCl_4$ (0.5 mL), the band of 450 nm decreased, while the band of 700 nm increased and redshifted. For Sample d, the band at 400 nm nearly disappeared and the absorption peak shifted to ~800 nm. The shift in peak location was attributed to the increase in void size and the reduc-

[a]Author to whom correspondence should be addressed; electronic mail: songhongwei2000@sina.com.cn

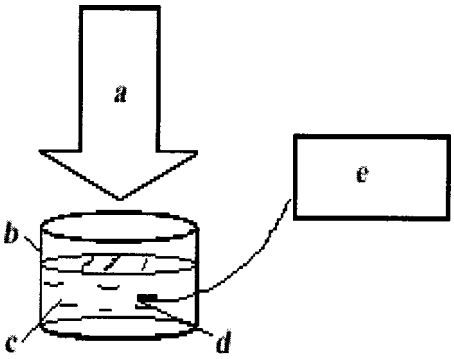

FIG. 1. Experimental setup for the measurements of photothermal transfer: (a) 800 nm laser, (b) culture dish, (c) gold nanoshells hydrosol, (d) thermal detector, (e) thermal detect controller.

tion in wall thickness for the shells.[1] The spectral changes were consistent with the formation of seamless Au nanoshells. For Sample e, a band at 530 nm appeared, which was the characteristic surface plasmon band of gold.[1] As the $HAuCl_4$ solution is excessive, the gold nanoshells were destroyed and gold nanoparticles were formed.

It was reported that during the forming process of a gold nanoshell from silver nanospheres, the chemistry reaction of $Ag^+Cl^- \rightarrow AgCl$ occurred. For the solubility, the product of AgCl is raised with temperature due to a positive enthalpy for the dissolution process.[10] The silver chloride formed in this redox reaction should be completely soluble in water under our experimental conditions (100 °C, refluxed). This process can be observed by the following TEM images. Figure 3 shows TEM images of silver nanospheres before and after a reaction with different volumes of $HAuCl_4$. From Fig. 3(a), it can be seen that the silver resultants yield very smooth nanospheres with sizes of 10–20 nm. From Figs. 3(b) and 3(c), it can be seen that after these Ag nanoparticles reacted with $HAuCl_4$, nanoshells formed and Ag oxidized gradually. As shown in Fig. 3(b), there were some pinholes in the surfaces of the shells and some shells had cores in the middle (as labeled by an arrow). The cores were the silver nanospheres that were not oxidized and the pinholes were the channels by which the Ag^+ was effused out. Figure 3(c) demonstrates that with the increase of $HAuCl_4$, the silver was

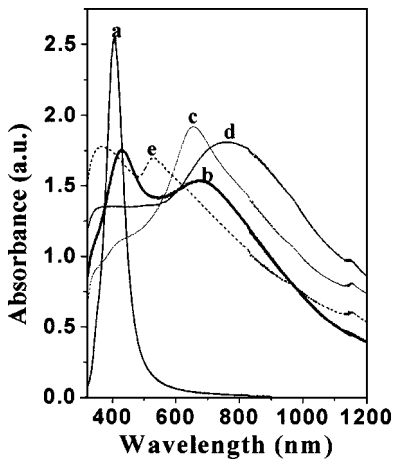

FIG. 2. UV-VIS-NIR absorption spectra of aqueous dispersions of silver nanospheres before and after a reaction with different volumes of 1 mM $HAuCl_4$ aqueous solutions: (a) 0 mL, (b) 0.3 mL, (c) 0.5 mL, (d) 0.7 mL, and (e) 1.0 mL.

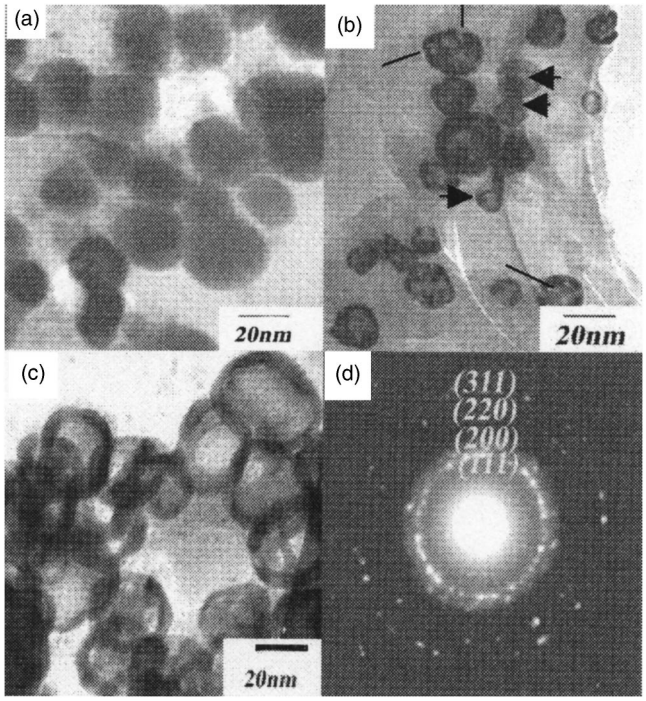

FIG. 3. TEM images taken from silver nanospheres before and after a reaction with different volumes of 1 mM $HAuCl_4$ aqueous solution: (a) 0 mL, (b) 0.5 mL, arrow point to core and line point to pinhole, (c) 0.7 mL, and (d) electron diffraction image of nanoshells.

exhausted. As the redox reaction was complete, the particles were hollow. The central portion of each Au particle was lighter than its edges as a result of their difference in electron attenuation. The reaction between Ag and $HAuCl_4$ led to the formation of gold shells around silver templates, and the size was consistent with the size of Ag particles. Note that the gold nanoshells exhibited a combination of morphologies similar to that of silver templates, and all shells in the product were characterized by smooth surfaces. The lattice constant was calculated from an electron diffraction pattern [see Fig. 3(d)], to be 4.078 Å. This value was in agreement with the JCPDS (Joint Committee on Powder Diffraction Standards) standard card (file no. 04-0784) and indexed to face-centered cubic.

Figure 4 demonstrates the temperature of the NIR-irradiated hydrosols containing Au nanoshells versus time. It can be seen that heating occurred immediately when the 808 nm laser irradiated the sample. Initially, a rapid temperature change occurred, followed by a gradual variation. Such a significant variation within a brief period was attributed to intense localized heating before thermal diffusion. It can also be seen that the longer the irradiation time and the higher concentration, the higher temperature change. The inset of shows Fig. 4 the temperature of the irradiated samples as a function of the concentration of gold nanoshells. It can be observed that the temperature linearly increased with the concentration, indicating that the absorption of the gold nanoshells hydrosol obeyed the Lambert–Beer law. In our experiments, the largest temperature increase (ΔT) reached 30 °C after the sample was exposed to the 808 nm diode laser for 12 min (with a power density of 5 W/cm^2). We believe that under the same laser exposure, the temperature will increase more if the gold nanoshells were injected into tissues because of the lower thermal diffusion velocity in the body. It is well known that tumor cells can be killed at

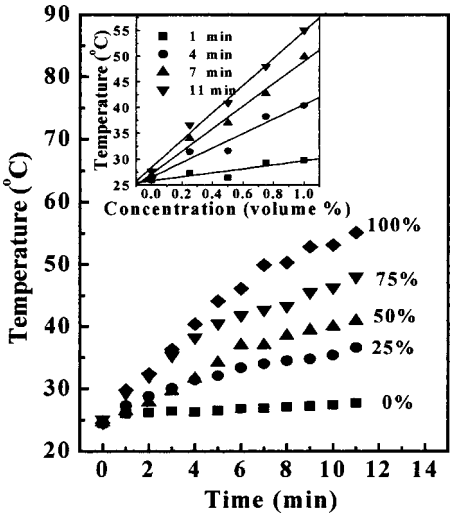

FIG. 4. Dependence of temperature of the NIR-irradiated hydrosols containing Au nanoshells on irradiation time. Inset: Temperature of the NIR-irradiated hydrosols containing Au nanoshells vs volume concentration.

$\sim$42 °C.[11] The tumor tissues injected with gold nanoshells may easily be heated from body temperature to $\sim$42 °C ($\Delta T \approx 5$ °C) in a short time. The special thermal properties of the gold nanoshells are promising for use as ideal photothermal converters in a range of applications including photothermal cancer therapy and photothermally triggered drug release.

In conclusion, Au nanoshells with excellent optical absorption and photothermal conversion properties were prepared, with a shell size of $\sim$20 nm. Their plasma absorption covered the visible and NIR regions. The temperature increase of the gold nanoshell hydrosol induced by photothermal conversion was as high as 30 °C. This material has promising use in the field of biomedicine.

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