

HOLLOW GOLD NANOSTRUCTURES PREPARED BY GALVANIC REPLACEMENT REACTION: SYNTHESIS AND OPTICAL PROPERTIES

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ABSTRACT

The synthesis of hollow Au nanostructures is described, using the galvanic replacement reaction with Ag nanoparticles as the templates. The effect of reaction conditions, including PVP concentration and reaction time on the morphology of the Ag templates was investigated. Using Ag nanocubic-shape templates, 50 nm hollow Au nanostructures were prepared. The results indicated that the plasmon resonance of the hollow Au nanostructures was strongly affected by the amount of Au precursor and could be tuned between 460 and 860 nm by simply altering the volume of the Au precursor solution from 0.5 mL to 3 mL. The hollow Au nanostructures were heated with an 808 nm laser (1.8 W), which showed that the sample temperature reached 55 °C after just 5 min irradiation. The ease of synthesis the hollow Au nanostructures with a plasmon peak in the near infrared of relatively small size and high capacity of conversion of photon energy into heat makes them a novel and promising material for photo-thermal and -imaging applications.

Keywords: hollow gold nanostructure, galvanic replacement, surface plasmon resonance (SPR).

1. INTRODUCTION

Gold nanostructures have received a great deal of attention due to their optical property known as localised surface plasmon resonance (LSPR) and their consequent potential in diverse applications in photonics, catalysis and biomedicine [1 - 6]. A variety of gold nanostructures with different sizes and shapes have been developed [1, 4 - 6]. Au spherical nanoparticles with the LSPR peak tuned between 510 and 600 nm have been most studied [2].

These spherical Au nanoparticles, however, are less useful in some *in vivo* biomedical applications where near-infrared light in the range of 650 - 1000 nm is preferred, due to its deeper penetration (both blood and soft tissues are more transparent in this range) [3]. As a result, other Au nanostructures, such as nanorods [13 - 16], nanoshells (dielectric core/gold shell) [1, 3, 6 - 9] and hollow nanostructures [1, 3, 10 - 12], which strongly absorb light in the near infra-red range have been intensively investigated [5, 13]. Amongst these, hollow Au nanostructures combine finely tuned optical properties, thermal stability and large surface area, including that inside the nanostructure, which provides potential for carrying protected payloads of, for example, drugs.

To date, a number of synthesis strategies have been developed for preparing hollow nanostructures, involving, for example, hard templates, soft templates, the Kirkendall effect, chemically induced self-transformation or galvanic replacement reaction [17]. The galvanic replacement approach is particularly interesting, due to the possibility to study the intricacies of alloying and de-alloying in metallic nanostructures and to its high tunability. In the latter respect, the galvanic replacement method is a simple method for precisely tailoring the structures and the resulting optical properties of these materials [17, 18].

In the current work, hollow Au nanostructures were prepared through a galvanic replacement reaction between Ag nanocubes templates and Au salt precursor. The influence of the volume of Au salt solution on the optical properties of the hollow Au structures was investigated and the photo-thermal effect of the hollow Au nanostructures under the irradiation of a near infra-red laser was also measured.

2. EXPERIMENTAL

2.1. Materials

Polyvinylpyrrolidone (PVP, $M_w \sim 55,000$ g/mol), Gold (III) chloride hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, 99.999 %), silver nitrate (AgNO_3 , 99.9 %) were ordered from Sigma-Aldrich, Singapore. Ethylene glycol (EG, 99 %), sodium sulphide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, ≥ 98 %), acetone ($\text{C}_3\text{H}_8\text{O}$, 99.5 %) were purchased from Merck. The deionised water was used for all experiments. All chemical were used as received without any purification.

2.2. Synthesis of Ag templates

Synthesis of Ag templates was carried out under oxygen-free conditions. In a typical synthesis, 108 mg PVP was dissolved in 15 ml EG in a three-necked flask immersing in an oil bath. The oil bath was then placed on a heating mantle equipped with a magnetic stirrer. The solution was heated to 170 °C and maintained at this temperature for 30 min to remove water. Na_2S in EG (80 μL at 1.54 mg/mL) and 1 mL EG containing 96 mg AgNO_3 were rapidly added into the flask in this order. The reaction mixture was maintained for different times (30 - 120 min) at 170 °C before cooling to room temperature. To purify sample, 15 mL acetone was added into the final reaction solution, the mixture was then centrifugated at 4,000 - 5,000 rpm for 5 min. The precipitated nanoparticles were re-dispersed in 15 mL deionized water. The purification process was repeated at least 3 times to remove excess reactants.

2.3. Synthesis of hollow Au structures

Hollow gold nanostructures were prepared via galvanic method by reaction of HAuCl_4 salt with Ag prepared nano-templates. In a typical synthesis, 1 mL solution of purified Ag sample

was diluted in 20 mL deionized water and placed in a three-necked flask on a magnetic stirrer. The solution was magnetically stirred and then slowly heated to 100 °C. At this temperature, a certain volume of gold salt solution made of 12 mg HAuCl₄ and 180 mg PVP dissolving in 18 mL deionized water was injected into the flask. After 10 min, the solution was cooled down slowly to room temperature.

2.4. Instrumentation

TEM (transmission electron microscopy) was done on a JEM 1010 (Japan) microscope. The UV-Vis spectra of samples were acquired on a Jasco V-670 (Japan) spectrophotometer. The photo-thermal effect was investigated on the home-built instrument, where the gold sample solution was irradiated with an 808 nm semiconducting laser at a power of 1.8 W.

3. RESULT AND DISCUSSION

3.1. Ag templates

It was well known that the optical properties of hollow Au nanostructures strongly depend on their morphology, which in the case of a galvanic replacement reaction is determined by the morphology of the Ag nanoparticles. Table 1 summarises the influence of the synthetic conditions used to prepare silver nanoparticles on the Ag particles' morphology.

Table 1. The effect of reaction conditions on the morphology of Ag nano-templates.

| Sample | PVP (mg) | AgNO ₃ (mg) | Time reaction (minutes) | Shape |
|----------|----------|------------------------|-------------------------|-------------------|
| STO1-30 | 54 | 96 | 30 | rod, sphere |
| STO1-60 | | | 60 | rod, sphere |
| STO1-90 | | | 90 | Sphere |
| STO1-120 | | | 120 | Sphere |
| STO2-30 | 108 | 96 | 30 | Sphere |
| STO2-60 | | | 60 | Rod |
| STO2-90 | | | 90 | cube |
| STO2-120 | | | 120 | cube |
| STO3-30 | 162 | 96 | 30 | sphere |
| STO3-60 | | | 60 | sphere |
| STO3-90 | | | 90 | sphere, rod, cube |
| STO3-120 | | | 120 | cube, sphere |

It can be seen that the experimental parameters, including PVP amount and reaction time strongly affect the shape of Ag nanoparticles. For example, at the lower polymer amount of 54 mg PVP, a mixture of rod and spherical-like Ag nanoparticles was obtained with reaction times of 30-60 min and solely spherical-like shapes after 90-120 min reaction (Table 1 and Figure

a.1-4). At the higher polymer amount of 108 mg PVP, Ag nanoparticles with different shapes were observed depending on the reaction time (Table 1 and Figure b.1-4). Spherical-like (strictly faced shape) Ag nanoparticles formed at the initial stage of the reaction then developed into rod-like shape after 60 min. By prolonging the reaction time to 90 and 120 min, Ag nanocubes were obtained. By increasing the PVP amount further to 162 mg, a similar trend in the morphological evolution of Ag nanoparticles was observed. Here, nanoparticles with faced shape were initially formed in the solution and these evolved into different shapes, including rods and cubes, depending on the reaction times (Table 1 and Figure c.1-4).

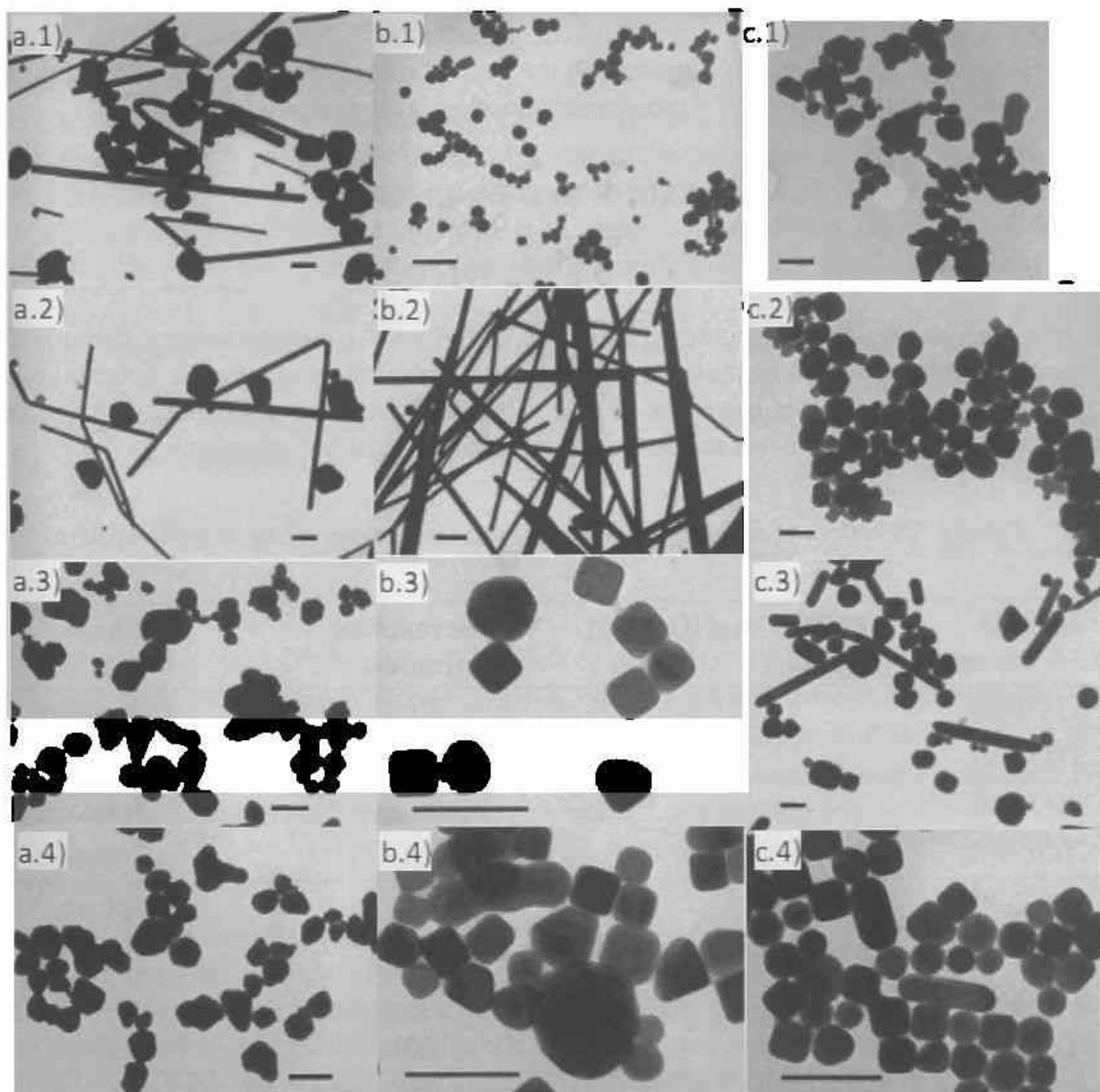


Figure 1. TEM images of Ag template prepared under different synthetic conditions: a.1-4) 54, b.1-4) 108 and c.1-4) 162 mg PVP with different reaction times: 30 (a-c.1); 60 (a-c.2), 90 (a-c.3) and 120 min (a-c.4). Scale bar: 100 nm.

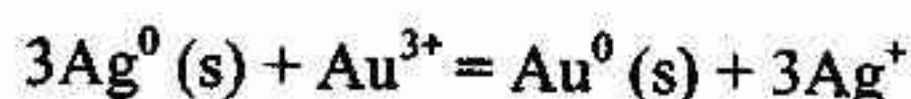
Morphological evolution of Ag nanoparticles with the reaction time was previously investigated by several authors [18,19]. According to Xia *et al.*, the reduction of Ag^+ by ethylene glycol (EG) at high temperature produced small twinned Ag nuclei [19], which usually favour for the formation of nanorods. In the presence of an etchant (oxygen, chloride or sulfide), the rods are then rapidly dissolved leading the re-formation of single-crystal seeds, preferential for the growth of Ag nanocubes. Thus, an explanation for how our syntheses

generate nanorods is that small faceted twinned nanoparticles were formed in the solution at the initial stage of the synthesis, which triggered the subsequent formation of nanorods.

By extending the reaction time, the nanoparticles grow. However, in the presence of sulfide as an etchant, the twinned nanorods will be dissolved due to the selective etching property of Ag nanoparticles (twinned Ag NPs are more easily etched than single-crystal ones) releasing abundant monomer (Ag atoms) in the solution, which lead to a secondary nucleation and then growth of the nanoparticles with different shape depending on the PVP concentration. At the medium polymer amount (108 mg), PVP molecules are assumed to preferentially attach to the lowest energy {100} facets and inhibited further on these. In contrast, the other facets, particularly {111}, continue to grow, resulting in the formation of nanocubes. At the lowest PVP amount (54 mg), the PVP layer is not dense enough to reduce the growth on the {100} facets, thus leading to spherical or faced shape nanoparticles. However, under the highest polymer amount of 162 mg, PVP molecules are excessive in the solution, which prevent the nanoparticles grow in a particular direction and as a result, faced-shape nanoparticles. In fact, mainly faced- and a few rod-shape nanoparticles are observed in TEM images (Figure c.1-3) after 30 - 90 min reaction.

3.2. Au hollow structures

Gold hollow nanostructures were synthesized through the galvanic replacement reaction using silver nanoparticles as templates. The chemical reaction involved in the galvanic replacement process is the following:



Here, Ag nanoparticles serve as both reducing agent and templates to produce the hollow Au nanostructures. Their size, shape and monodispersity will determine the morphology of the hollow nanostructures and so their optical properties. These parameters can be controlled by the Au^{3+}/Ag concentration ratio.

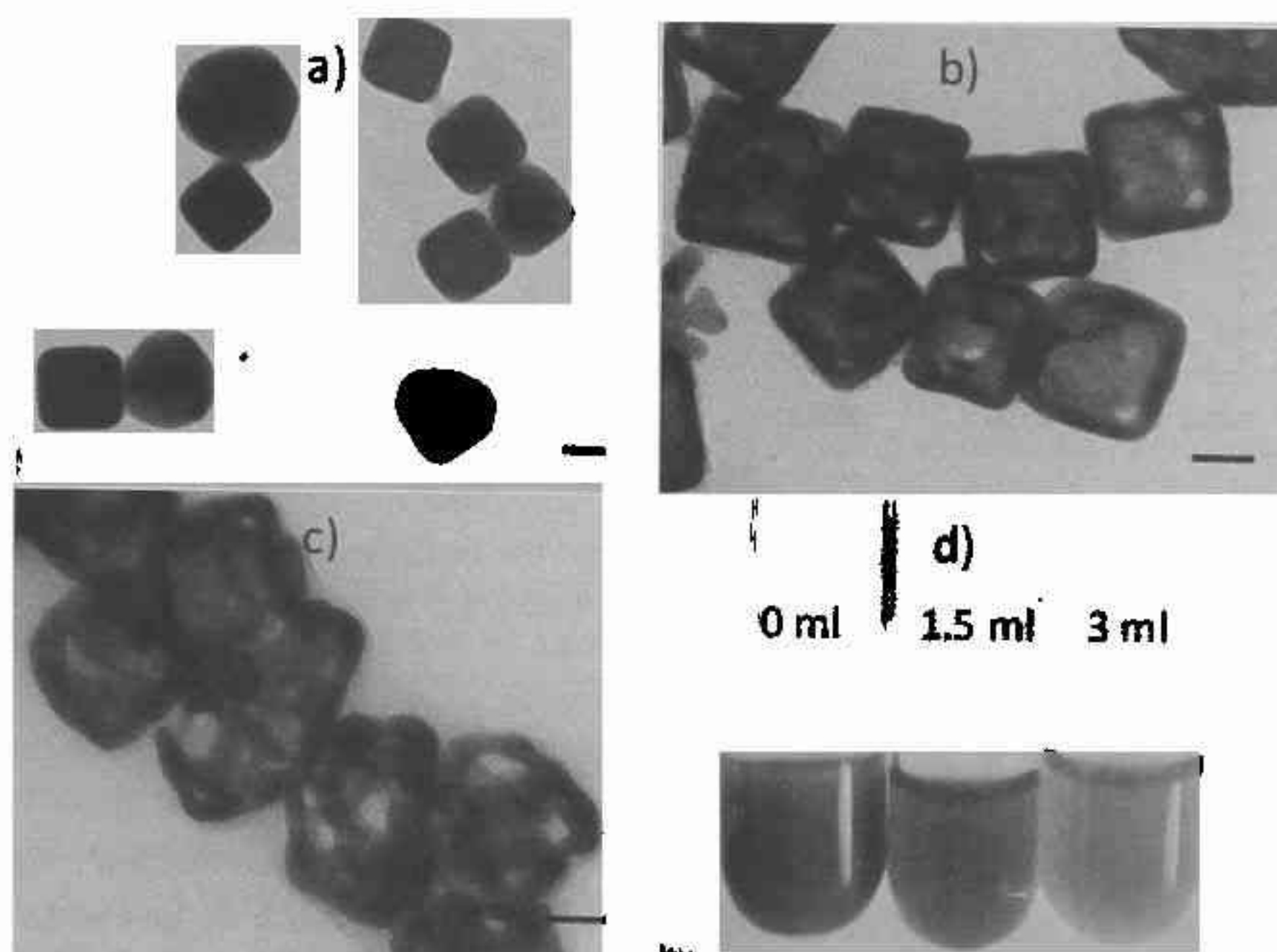


Figure 2. TEM images of Ag nano-templates (a) and the hollow Au nanostructure prepared at 1.5 (b), 3 mL(c) HAuCl_4 solution. Scale bar: 20 nm.

Figure 2 shows examples of hollow Au nanoparticles prepared with different volumes of gold salt solution when using Ag nanocubes as templates. It can be seen that the obtained Au nanoparticles have a cubic shape, similarly that of the Ag templates. At the edge of the Au nanoparticles for both samples prepared at 1.5 mL and 3 mL gold salt solution, the mass contrast is darker than inside, which suggests the formation of hollow nanostructures. The formation of the hollow Au nanoparticles was also evidenced by the pale blue or grey colour of Au solutions (Figure 2d) instead of the red colour displayed by conventional gold colloids or light brown of the template Ag colloid solutions. The size of the hollow Au nanostructure is about 50 - 60 nm, similar to that of the Ag templates, with a wall thickness of ~7 nm. In addition, the presence of several light areas inside the particles suggests the existence of open channels between the void and surfaces of the hollow Au nanoparticles.

3.3. Optical properties

Figure 3 shows the absorption UV-vis spectra of Ag nanocubic-shape template and hollow Au samples synthesised with different volumes of HAuCl_4 solution. It is clear that the plasmon resonance depends on the volume of gold salt solutions used. The 50 nm Ag nanocubic template (Figure 2.a) has an initial plasmon peak at 425 nm. When a small volume of gold salt solution (0.5 mL) was added, the plasmon peak was red-shifted to 465 nm. Increasing the volume of gold salt solution to 1.5 mL, resulted in the plasmon peak at 762 nm and with 3 mL gold salt solution this peak red-shifted to 860 nm.

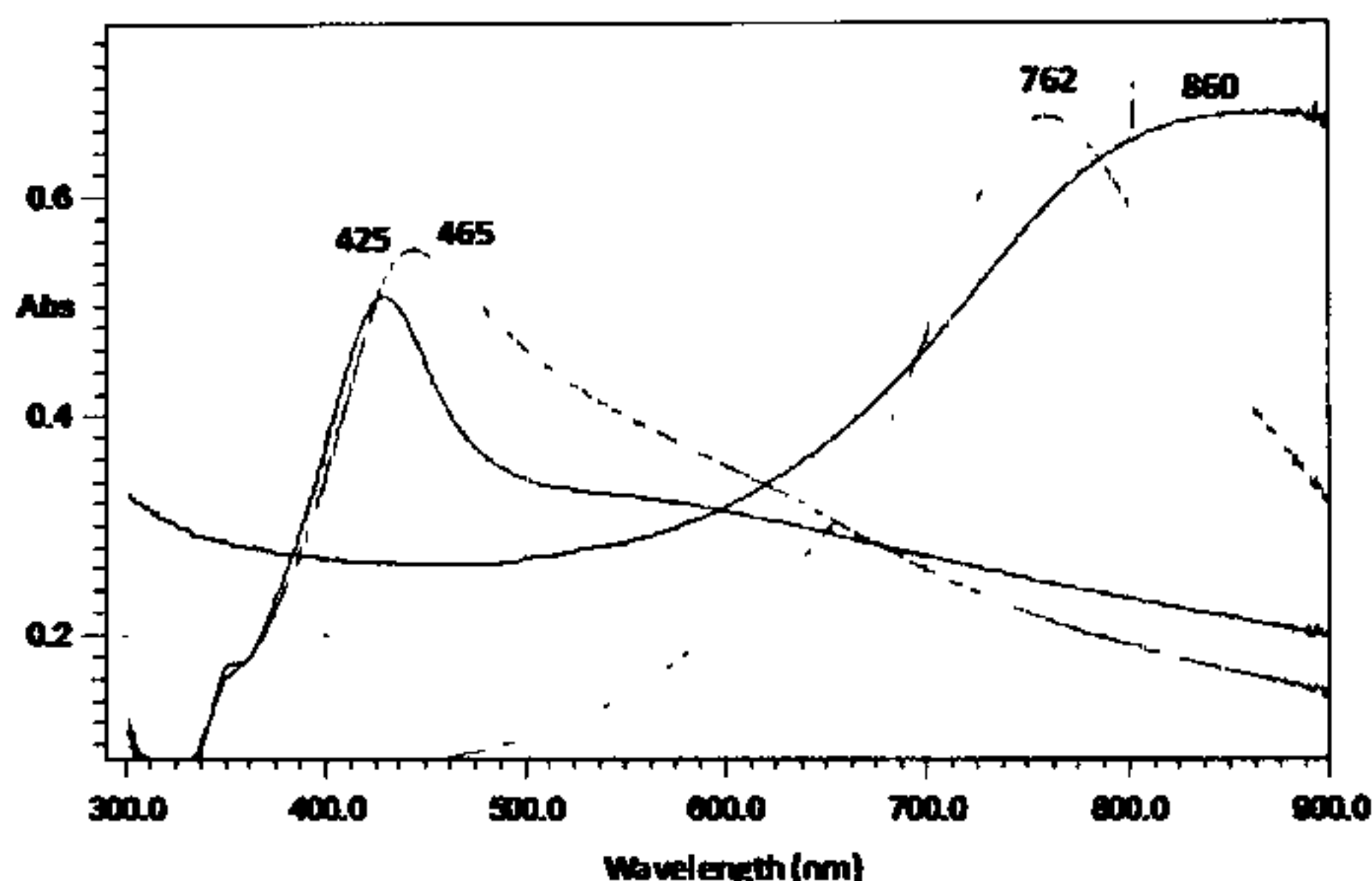


Figure 3. UV-vis spectra of Ag nanocubes (blue) and the hollow gold samples synthesized with different volumes of HAuCl_4 solution: 0.5 mL (red), 1.5 mL (pink) and 3 mL (black).

3.4. Photo-thermal effect of hollow Au nanostructures

One of the most interesting potential applications of gold hollow nanoparticles is hyperthermia treatment of cancer. Tumor cells are known to be more sensitive to a temperature increase than normal cells. Heating tumor cells to a temperature of 42 - 46 °C will fatally damage the cells. Moreover, hyperthermia seems to modify the surface of the cell, such that

they are easier recognised by the immune system. In the current study, to evaluate the potential of the hollow gold nanoparticles for photo-thermal cancer therapy we investigated the photo-heating effect of the gold nanoparticles under near infra-red laser irradiation. Around 0.2 mL solution was irradiated with an 808 nm diode laser (power 1.8 W) and the temperature change was recorded by a temperature sensor (PT100) immersed in the solution. The experimental setup for heating Au colloidal solution was illustrated in Figure 4.

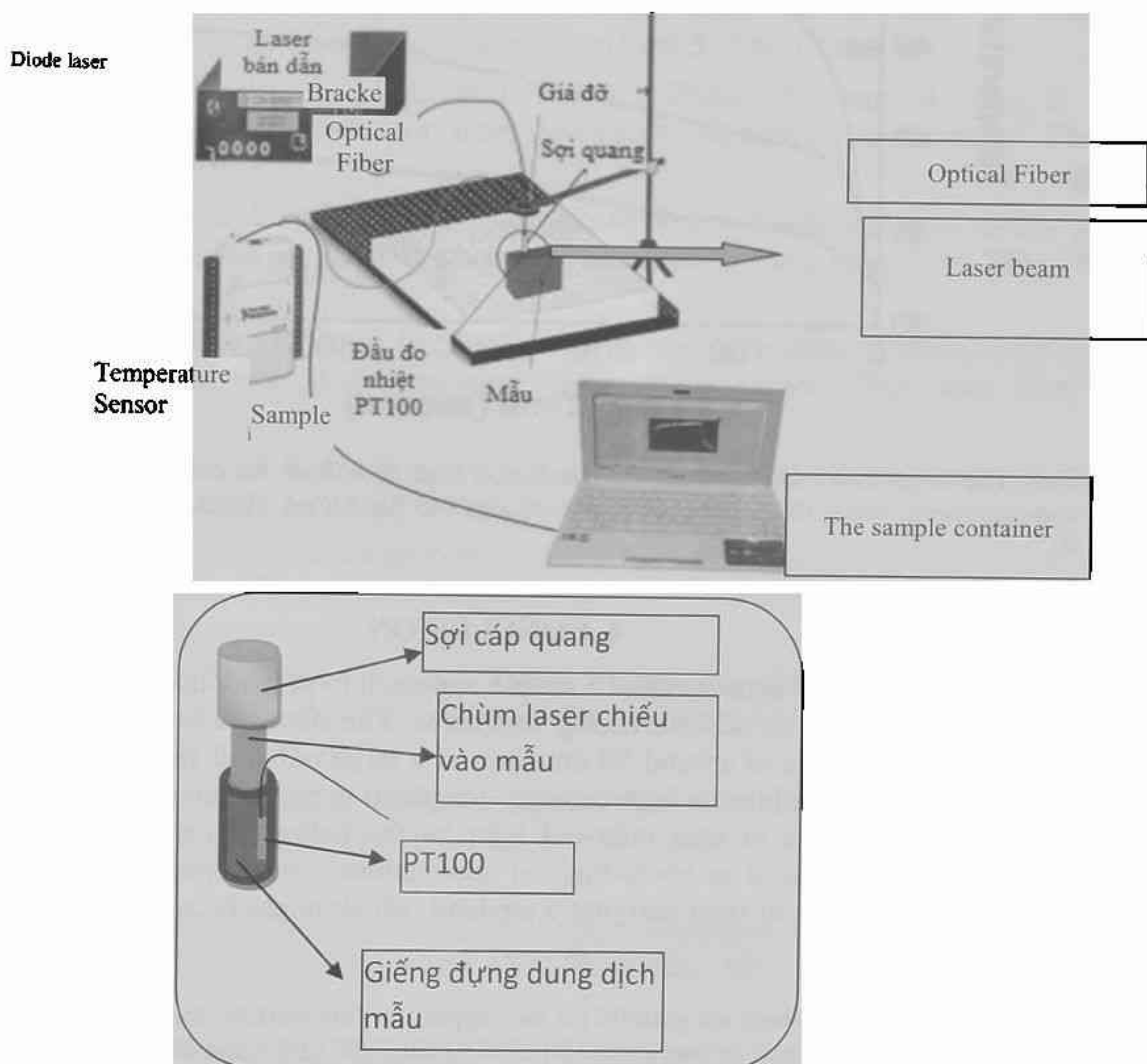


Figure 4. Illustration of experimental setup for heating hollow Au nanostructures using an 808 nm diode laser.

Figure 5 shows the temperature change with the irradiation time of the samples prepared at the different hollow Au nanoparticle concentrations. For a control water sample, a small change in the temperature from 32 °C to 37 °C was recorded after 10 min irradiation. At 40 µg/mL Au of hollow nanoparticles, the solution temperature increased to 40 °C after 2 min and reached a maximum of 43 °C after about 6 min. At higher Au concentrations (165 µg/mL of hollow Au nanostructures), a sharper increase in temperature was observed. The solution temperature reached 45 °C after just 30 s and a maximum value of 55 °C after 5 min irradiation.

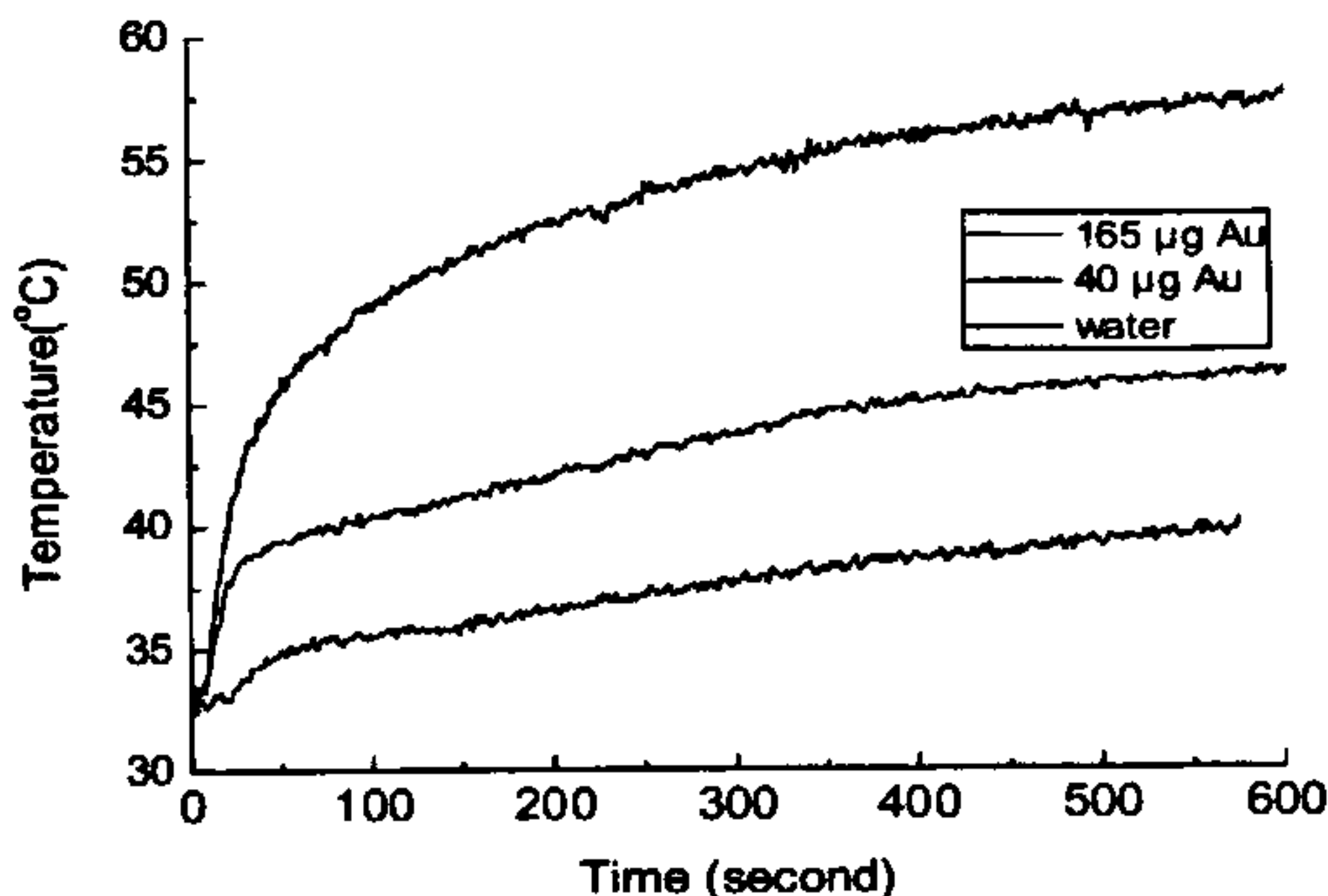


Figure 5. The temperature change with the irradiation time of hollow Au colloidal solution at different Au concentrations: water (blue line), 40 (red line) and 165 µg Au/mL (black line). Power of the laser is 1.8 W.

4. CONCLUSION

We have successfully demonstrated a simple approach to prepare hollow Au nanostructures utilizing Ag nanocubes as self-sacrificing templates. The obtained hollow Au nanoparticles with relatively small size of around 50 nm showed a large red-shift their plasmon absorption peak to 860 nm and exhibited a high capacity for photo-thermal conversion of 808 nm light. The effective conversion of near infra-red light by the hollow Au nanostructures into heat demonstrates their potential in photo-thermal applications. Since these materials are hollow, they open the possibility of their carrying a payload, which might be activated by local photo-thermal heating.

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TÓM TẮT

TỔNG HỢP VÀ TÍNH CHẤT QUANG CỦA CẤU TRÚC VÀNG RỒNG CHẾ TẠO BẰNG PHƯƠNG PHÁP THỂ GALVANIC

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Bài báo trình bày nghiên cứu chế tạo hạt nano Au rỗng bằng phương pháp thể galvanic sử dụng template là các hạt nano Ag. Ảnh hưởng của điều kiện thực nghiệm như nồng độ PVP và thời gian phản ứng đến kích thước, hình dạng và độ đồng đều của hạt nano Ag đã được tiến hành khảo sát. Sử dụng hạt nano Ag hình lập phương làm template, chúng tôi đã chế tạo thành công hạt nano vàng rỗng có kích thước 50 nm. Kết quả thu được cho thấy đỉnh cộng hưởng Plasmon của hạt Au rỗng bị ảnh hưởng rất mạnh bởi lượng muối vàng sử dụng và có thể điều khiển trong khoảng 460 nm đến 860 nm khi thay đổi lượng muối vàng sử dụng từ 0.5 mL lên 1 mL. Hạt vàng rỗng có thể được đốt nóng bằng việc sử dụng laze hồng ngoại có bước sóng 800 nm (công suất 1.8 W), nhiệt độ cực đại của mẫu đạt được là 55 °C chỉ sau 5 phút chiếu laze. Điều này cho thấy các hạt vàng rỗng có tiềm năng ứng dụng to lớn trong lĩnh vực quang nhiệt trị hoặc chụp ảnh quang trong y sinh.

Từ khóa: cấu trúc vàng rỗng, phản ứng thể galvanic, cộng hưởng bề mặt plasmon.