A novel method to prepare Au nanocage@SiO_2 nanoparticle*

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Gold (Au) nanocage@SiO_2 nanoparticles are prepared by a novel approach. The silver (Ag) nanocube@SiO_2 structure is synthetized firstly. Next, the method of etching a SiO_2 shell by boiling water is adopted to change the penetration rate of $AuCl_4^-$ through the SiO_2 shell. $AuCl_4^-$ can penetrate through silica shells of different thickness values to react with the Ag nanocube core by changing the incubation time. The surface plasma resonance (SPR) peak of synthetic Au nanocage@SiO_2 can be easily tuned into the near-infrared region. Besides, CdTeS quantum dots (QDs) are successfully connected to the surface of Au nanocage@SiO_2, which testifies that the incubation process does not change the property of silica.

Keywords: Ag nanocube, Au nanocage, silica, nanostructure

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1. Introduction

Gold (Au) nanocages have been particularly attractive in the last few years, because of their large absorption cross-sections and their tunable surface plasma resonance (SPR) peak. Especially, their SPR can be easily tuned into the near-infrared (NIR) region,[1,2] where the attenuation of light by blood and soft tissue is greatly reduced.[3,4] Hence, Au nanocages are well suited for being used as a photothermal material.[3,4] Au nanocages covered by smart polymers can be used to control the release of the pre-loaded effector with near-infrared light.[5] Poly (ethylene glycol)-coated Au nanocages are evaluated as a potential NIR contrast agent for photoacoustic tomography (PAT).[6]

Usually, silver (Ag) or Au nanoparticles are easily oxidized in air and aggregated in a solution containing salt. To overcome these shortcomings, coating one layer on metal nanoparticle has been considered.[7] Silica is chemically inert in a variety of solvents and highly transparent across a wide range from the infrared to visible spectrum,[8] which makes it a suitable material for forming core-shell nanoparticles. Metal@SiO_2 core-shell nanostructure has attracted much attention, because of its interesting chemical and physical properties and its potential application in metal enhanced fluorescence (MEF)[9,10] and photothermal therapy.[3] The wet chemical process deposited silica has a lot of virtues. Many groups have adopted the method to coat a silica shell around a core nanoparticle to reduce the chemical toxicity[11] and stabilize the surface of the core particle,[7,12] without damage to the optical properties of the core.[8] Silica coated Au nanoparticles can also be used to control the distance between Au core nanoparticles and quantum dots (QDs) through the shell thickness.[9,13] In addition, the problem of the surface functionalization of Au nanoparticles is perfectly solved. A silica shell helps to tailor the surface properties of the Au nanoparticles for further bilconjugation.[8] This core-shell structure can be functionalized with amino, carboxyl, and alkyl groups to facilitate the rapid translation of the nanoparticles to the target location.[7,8,13–16] Some functional nanoparticles, such as QDs, can be connected via these groups, which combine the photothermal properties of the Au nanocage with the optical properties of QDs, showing the potential application in biological mark treatment. A new trend in current nanobiotechnology and theranostics is the fabrication of multifunctional nanoparticles, which combine the therapeutic and diagnostic modalities in a single nanostructure.

In the past few years, Chen *et al.*,[3] Siekkinen *et al.*,[17] and Chen *et al.*[18] have done excellent work on synthesis of the nanocube. Recently, Khlebtsov *et al.*[14] reported on the composite structure of the Au nanocage@SiO_2. In these studies, the Au nanocage was firstly synthesized and then a silica shell was coated around the nanocage core. However, there is great loss in the synthesis process and the coated silica shell is inhomogeneous due to the use of this method.

In this paper, we further explore the Au nanocage@SiO_2 core-shell structure using a new method. We break the routine to synthesize the composite nanoparticle from the outer to the inner circle. The product is a Ag nanocube@SiO_2 in this middle process, but not a Au nanocage that is the product of the previous method. Obviously, this new method will have less loss in the washing process, because Ag@SiO_2 nanoparticles are much heavier than the Au nanocage, on the condi-

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tion that their nanoparticle numbers are the same. In addition, SiO_2 is easier to deposite around a Ag than a Au nanocage. So, the synthesis becomes easier and more productive. The product still retains the similar optical properties to those of the Au nanocage. In the meantime, a silica shell is fabricated around the Au nanocage core so that we can modify the surface by adding some silane coupling agents to terminate the silica surface with amino. Carboxyl-terminated CdTeS QDs are assembled onto the surface of amino-terminated Au nanocage@SiO_2 by the electrostatic attraction technique. The Au nanocage@SiO_2@CdTeS QD nanocomposites are synthetized. The Au nanocage yolk-shell structures are synthesized in the process of exploration. This structure can be used as an excellent drug carrier.[19]

2. Experiment

2.1. Materials

In this work, the following materials are used: ethylene glycol (EG) (99.0%), poly(vinyl pyrrolidone) (PVP, powder, $M_w \approx 5.5 \times 10^4$), NaHS, $AgNO_3$, acetone (99.5%), Ethanol (99.7%), deionized water (18.25 MΩ·cm^{-1}), chloroauric acid , sodium chloride (NaCl) crystal ($> 99.\%$), tetraethyl orthosilicate (TEOS) (28.4% SiO_2, AR), ammonia (25%–28% NH_3, AR) and 3-aminopropyltrimethoxysilane (APS, Sigima) (98%), where AR stands for the analytical reagent.

2.2. Preparation of Ag nanocube

The sulfide-mediated polyol method was used to prepare Ag nanocubes.[2] A 6-ml EG was pipetted into a reaction vial and heated in an oil bath at 150 °C for 1 h with stirring. 100-μL NaHS (3 mM in EG) was quickly poured into the vial. 8 min later, 1.5-ml PVP (0.18 M in EG) was added, 2 min later, 0.5 mL $AgNO_3$ (0.28 M in EG) was added into the vial. About 20 min later, a green-red-colored reaction medium was observed. The vail was placed into water to suspend the reaction. Once the reaction solution cooled, 1-ml reaction solution and 3-ml acetone were pipetted into a 5-ml centrifuge tube. The product was spined down at 6900 rpm for 15 min. After removing and discarding the supernatant, the precipitate was rinsed once with ethyl alcohol and three times with pure water or ethyl alcohol. Finally, the product was dispersed in pure water or ethyl alcohol for further application.

2.3. Preparation of Ag nanocube@SiO_2

Ag@SiO_2 particles, with different silica thickness values, were prepared according to the Stöber method.[12] 40 ml of ethanol, 8 ml of water, and 0.8 ml of an ammonia aqueous solution were mixed under stirring. A 6-ml as-prepared Ag ethanol solution was dispersed into the mixture. Then 200 μl of TEOS was dissolved in 20-ml ethanol for subsequent synthesis. 400-μl TEOS ethanol solution was added slowly with continuous stirring once an hour. The reaction continued for 24 h. The silica thickness can be tuned by changing the amount of TEOS and the time of the reaction. The Ag@SiO_2 particles were separated by centrifugation and the supernatant was removed and discarded. Then, the product was rinsed twice with deionized water and dispersed in 16 ml of deionized water.

2.4. Preparation of Au nanocage@SiO_2

Au nanocage@SiO_2 composite particles were synthesized by a galvanic replacement reaction.[2] The 10 ml of PVP aqueous solution (1 mg of PVP was dissolved in 1 ml of pure water) and 4-ml as-prepared Ag nanocube@SiO_2 (or Ag nanocube) were pipetted into a 50-ml round bottom flask. This mixture was heated to 100 °C in the oil bath and was incubated for a certain time.[20] Then a specific amount of 0.2-mM $HAuCl_4$ (0.5 ml, 1 ml, 2 ml, 3 ml, and 4 ml) was added drop by drop into the solution under stirring. The mixture was refluxed for about 20 min in order to make the Ag nanocube react with added $HAuCl_4$ absolutely. Excess NaCl was added into the resulting solution until saturation. Then the products were centrifuged twice with deionized water. Finally, the precipitate was redispersed in 10 ml of an ethanol solution.

2.5. Preparation of Au nanocage@SiO_2@CdTeS QDs

Au@SiO_2 can be used to synthesize a complex composite structure. CdTeS QDs were synthesized by a very mature method, the emission wavelength of CdTeS QDs can be tuned by changing the reaction time.[21] To fabricate Au nanocage@SiO_2@CdTeS nanocomposites, Au nanocage@SiO_2 particles were treated with APS (a silane coupling agent),[22] in order to make silica surfaces functionalized with the –NH_2 group. The 100-μl APS was added into 10 ml of the Au nanocage@SiO_2 ethanol solution. The solution was continuously stirred for 12 h at 60 °C. Then the supernatant was removed and discarded by centrifugation. The precipitate was dispersed in 10 ml of deionized water. Next, 2-ml CdTeS QDs were added into the above solution and stirred for 6 h. The products were then centrifuged and rinsed three more times with water. Finally, the product was dispersed with water for further characterization.

2.6. Characterization

The morphology of the nanoparticle was investigated by transmission electronic microscopy (TEM, JEOL, JEM-2010) and a scanning electron microscope (SEM, JSM-6700F). The element analysis was conducted with energy dispersive spectroscopy (EDS). The UV-visible absorbance spectra were obtained using a UV-3600 UV-VIS-NI spectrophotometer. Photoluminescence spectra were measured using an F-4600 fluorescence spectrophotometer.

3. Results and discussion

Figure 1(a) summarizes the process of the formation of silica coated Au–Ag nanocages. A simple galvanic replacement reaction happened between the chloroauric acid and the Ag nanostructures. Firstly, Ag nanocubes were synthesized by a polyvinylpyrrolidone (PVP) protected method. Next, SiO_2 was deposited on Ag nanocubes using base-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS). When adding less TEOS, the shapes of the inner SiO_2 shell and the outer SiO_2 shell are both cubic. With the increase of TEOS, the outer SiO_2 shell became spherical due to surface tension. The kinetics of these Ag core reactions with $HAuCl_4$ solution reagents is governed by their rate of diffusion through the silica shell.[23] It was found that the rate of diffusion can be changed by the method of incubation. So the third step was to dig small burrows in the sillica shell via boiling the solution. Finally, the Au nanocage@SiO_2 composite nanoparticles were synthesized via alloying and dealloying. The resulting Au was deposited epitaxially on the surface of the Ag nanocubes, while the interior Ag is oxidized and removed. The detailed procedure is represented below.

Figure 1(b) shows that Au nanocage@SiO_2 nanoparticles were modified by APS to terminate the silica surface with amino groups. The negatively charged MPA-capped CdTeS QDs were electrostatically assembled on the surface of silica.

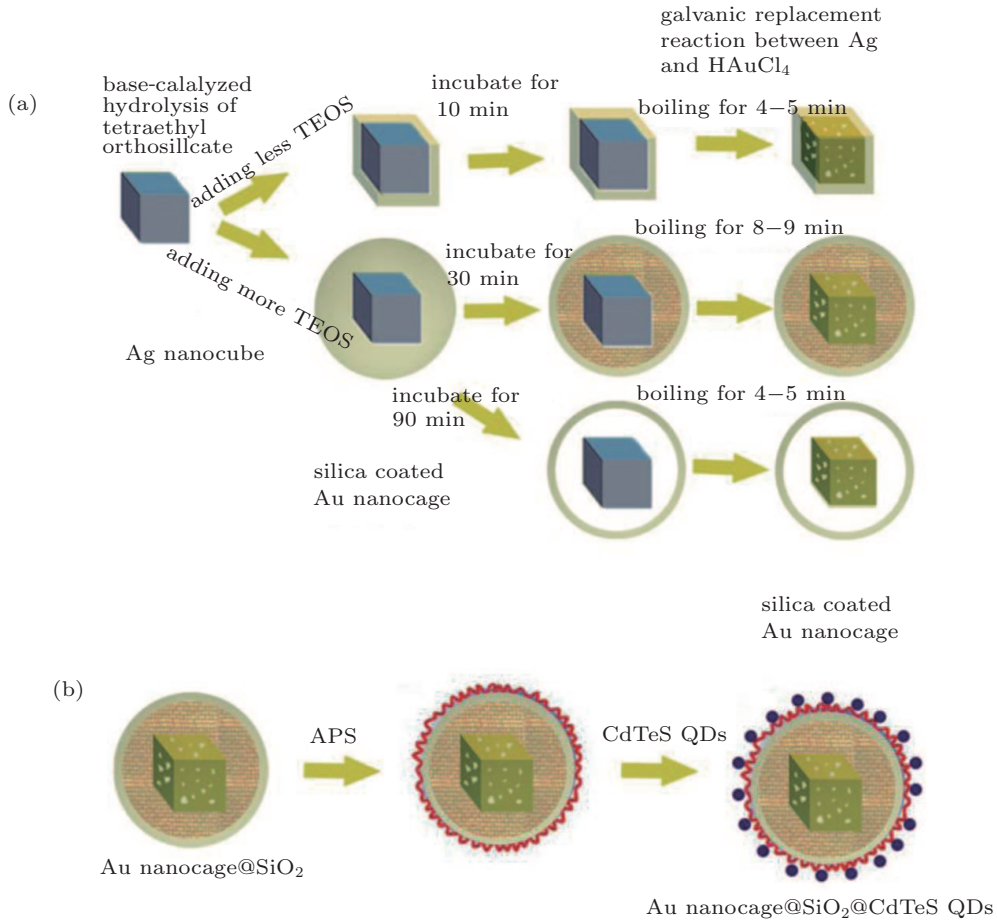


Fig. 1. (color online) (a) Illustrations of the preparation of the Au@SiO2 composite nanoparticle and (b) the preparation process of Au nanocage@SiO_2@CdTeS QDs.

The SEM (Fig. 2(a)) and TEM (Fig. 2(b)) images clearly demonstrate that the Ag nanocubes are highly uniform in particle size and shape distribution. Figures 2(c), 2(d), and the inset in Fig. 2(d) respectively show typical TEM images of Au nanocages of different SPR peaks, which were produced by adding different amounts of $HAuCl_4$ into the as-prepared Ag nanocubes.

In this paper, we use Ag nanocube@silica as a sacrificial template to generate a Au nanocage@SiO_2. When the silica shell is thin, it has little influence on the galvanic replacement reaction between the Ag nanocube core and $HAuCl_4$. $AuCl_4^-$ ions can easily penetrate through the silica shell and react with the inner Ag nanocube. As the thickness of the SiO_2 shell increases, $AuCl_4^-$ ions will encounter a block. The Ag@SiO_2 water solution did not show a series of color changes after adding the $HAuCl_4$ solution, which illustrates that $AuCl_4^-$ ions

cannot penetrate through the thicker SiO_2 to reach the position of the Ag nanocube. In order to reduce the block, the etching method was used for controlling the permeability. After incubation for some time, it was found that $AuCl_4^-$ can penetrate though these thicker SiO_2 shells as if there was no barrier, of which the mechanism is that small holes are created on the silica shell under a boiling temperature, which can introduce the $AuCl_4^-$ to permeate through the silica shell to interact with the Ag nanocube. The inner shell of SiO_2 was preferentially etched. After incubating for an appropriate time, the yolk-shell nanostructure of the Au nanocage@SiO_2 can be synthesized. Figure 3(a) shows the TEM images of the Ag nanocube (60 ± 5 nm)@SiO_2 (35 ± 5 nm). When the Ag nanocube@SiO_2 structure was boiled for 90 min, the inner layer of the shell was etched, but the outer layer remained unchanged. Without the inner layer, some silica shells collapsed (Fig. 3(c)). The inner layer of the shell had no evident phenomenon of corrosion for the Ag@SiO_2 structure, which was incubated in water at 100° for 30 min (Fig. 3(b)). But $AuCl_4^-$ can penetrate through the shell to react with the Ag core without a block. The reason should be that the silica shell was etched into a shell with many dinky holes. After being incubated for a shorter time (< 10 min), Ag@SiO_2 (the thickness of the SiO_2 shell > 30 nm) water solution did not present a series of color changes after adding the $HAuCl_4$ solution. Ag@SiO_2 must be incubated to generate burrows first. Then $HAuCl_4$ was added to produce a galvanic replacement reaction. Changing the time of incubation was used to improve the control of the permeability. The same amount of $HAuCl_4$ was added into the Ag nanocube@SiO_2 (35 nm) solution that was incubated for 30 min (90 min). When the solution has been boiling for at least 8 min–9 min (4 min–5 min), the SPR peak of the product would be stable, which manifests the termination of the reaction. But enough $HAuCl_4$ was added into the Ag nanocube@SiO_2 (35 nm) solution that was incubated for less than 10 min, the SPR peak of the product hardly changed when the solution had been boiled for half an hour. These phenomena prove that the permeability will be improved with the increase of the incubation time so that the $AuCl_4^-$ can contact the Ag. As the thickness of the SiO_2 shell increases, the block will become more and more serious. So Ag@SiO_2 must be incubated for a longer time firstly. Figure 3(d) shows that QDs can be successfully connected to the surface of SiO_2. This confirmed that incubation process did not break the surface property of silica. The SiO_2 shell can be functionalized with the amino. Figure 3(e) shows the etching process of Ag@SiO_2. When adding excess $HAuCl_4$, the structure will become a cavity of SiO_2. Figure 4 exhibits the energy dispersive spectroscopy (EDS) image of a Au nanocage@SiO_2, which proves that $AuCl_4^-$ can penetrate through the SiO_2 to react with the inner Ag.

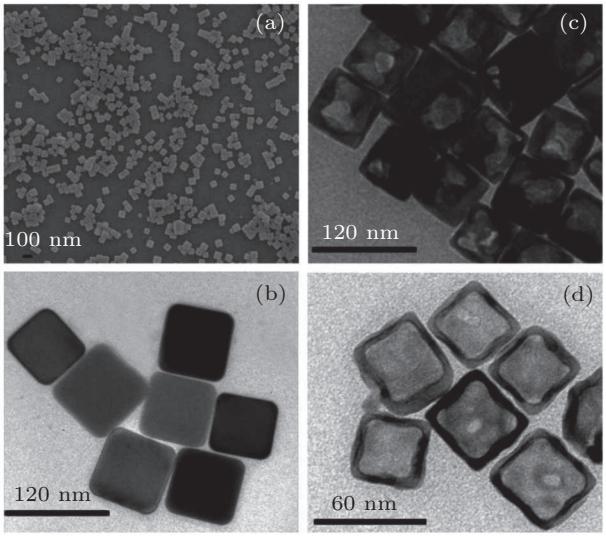


Fig. 2. (a) SEM image of a Ag nanocube; (b) TEM images of a Ag nanocube; (c) and (d) a Au nanocage (by adding different amounts of $HAuCl_4$).

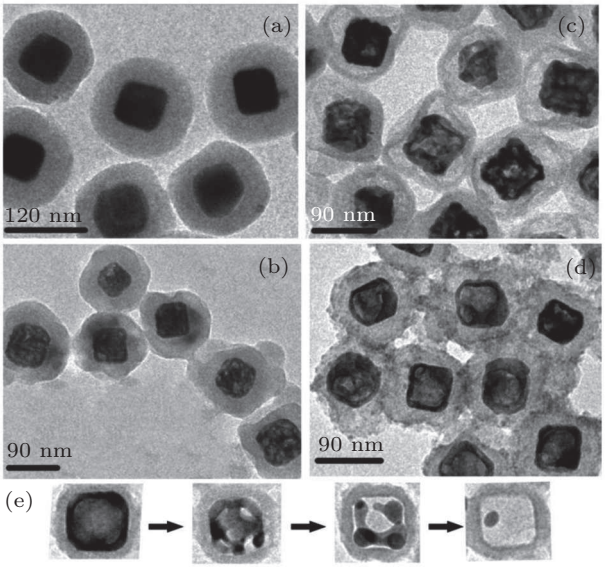


Fig. 3. TEM images of (a) a Ag nanocube@SiO_2 and a Au nanocage@SiO_2 incubated for (b) 30 min, (c) 90 min, (d) Au nanocage@SiO_2 (incubated for 30 min)@CdTeS QDs, (e) the corrosion process of Ag nanocube@SiO_2.

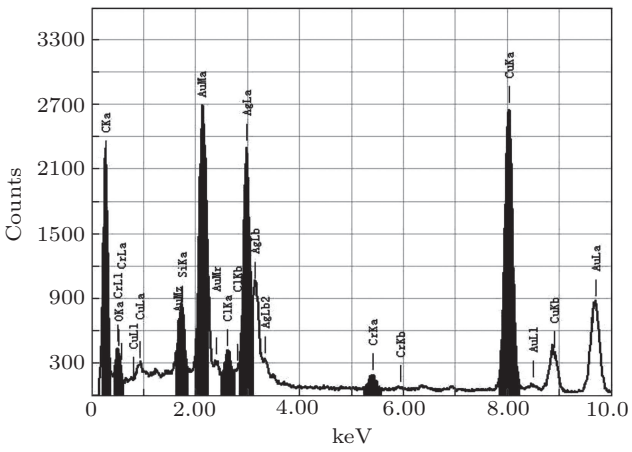


Fig. 4. EDS image of Au nanocage@ SiO_2.

The absorption spectrum of the Ag nanocube presents three main peaks. The left peak has both dipole and quadrupole resonance contributions, it is mainly the contribution of the dipole resonance mode; the middle peak corresponds to a quadrupole resonance mode; the right peak corresponds to a pure dipole mode.[24] As the nanocube size increases, the dipole resonance mode shifts toward higher wavelengths and the quadrupole modes become more intense,[25] as shown in Fig. 5(a). For the as-synthesized Ag nanocube, there are three kinds of colors contained in this colloidal solution as red, yellow, and green, which can be observed from different directions. The phenomenon is related to the three absorption peaks. Figure 5(c) reveals that the Ag nanoparticle@SiO_2 is slightly red-shifted compared with the absorption spectrum of the Ag nanoparticle. This is due to the change of the external dielectric surrounding the nanoparticles. The position and intensity of the surface plasma resonance peak depend on several factors, such as size, shape, morphology, composition of the nanoparticle, the dielectric environment around the nanostructure, crystallinity, etc.[24–26] The SPR of the Au nanocage is tunable in the visible and NIR region by varying the volume of the $HAuCl_4$ solution added (Fig. 5(b)). The absorption spectrum of the Au nanocage@SiO_2 demonstrates that the SPR peaks of the Au nanocage@SiO_2 can also be tuned to any position in the visible and NIR region by adding different amounts of $HAuCl_4$ to the reaction system. Figures 5(b) and 5(d) reveal that the SPR peaks of the Au nanocage@SiO_2 are similar to those of the Au nanocage. When adding 3-ml and 4-ml $HAuCl_4$ into the Ag nanocube solution, the SPR peaks of the product are 725 nm and 793 nm respectively, while adding 3-ml and 4-ml $HAuCl_4$ into the same amount of Ag nanocube@SiO_2 solution, the SPR peaks of the product are 785 nm and 850 nm, respectively. The SPR peaks of the Au nanocage@SiO_2 have a 63-nm red-shift compared with the corresponding Au nanocage, which is due to the change of the external dielectric surrounding, caused by the SiO_2 shell. Their SPR peaks can be easily tuned to the NIR region, no matter whether a SiO_2 shell exists. The optical properties of the Au nanocage are still retained, which proves that the Au nanocage@SiO_2 has the same potential usage in controlling the release of drugs, optical sensing, and photothermic therapy as the Au nanocage.[4] Figure 5(e) shows the images of the Au nanocage (the upper) and the Au nanocage@SiO_2 (the lower). Their color changes are similar after adding different amounts of $HAuCl_4$. Figure 5(f) shows that the fluorescence peak of the CdTeS QD has a slight red-shift after being assembled onto the surface of the amino-terminated Au nanocage@SiO_2 by electrostatic attraction.

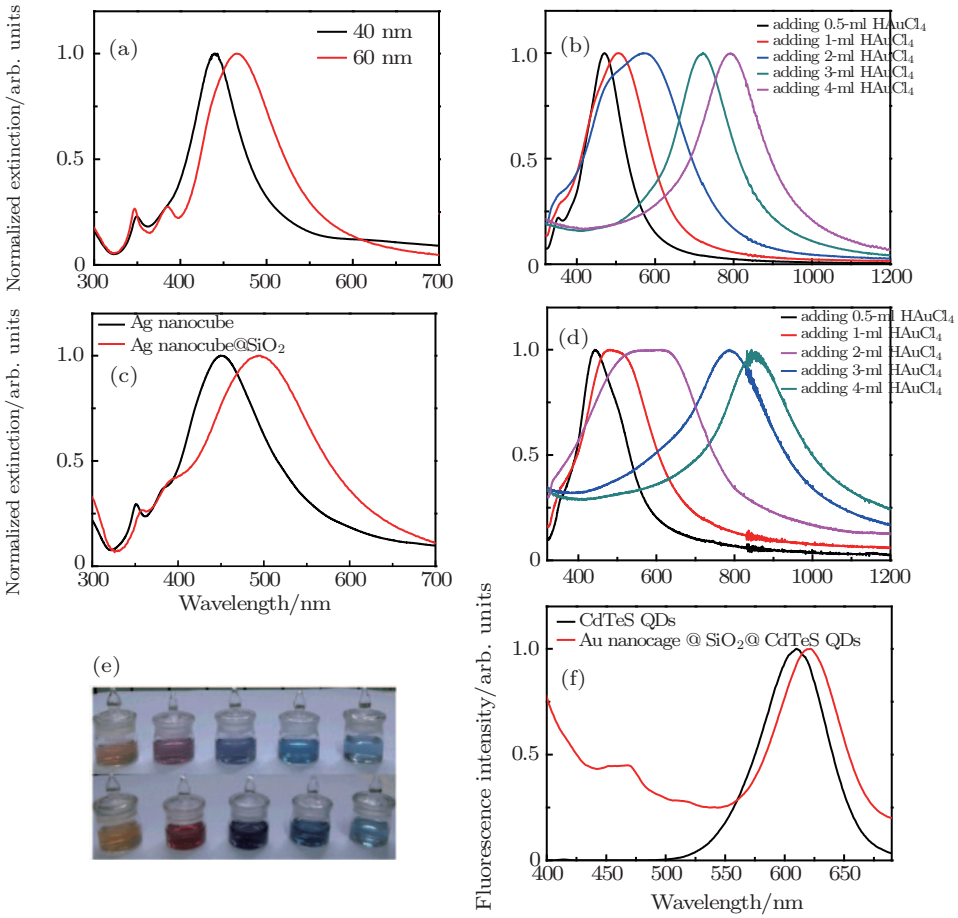


Fig. 5. (color online) The UV-visible absorbance spectra taken from (a) Ag nanocube of average sizes 40±5 nm and 60±5 nm, (b) Au nanocage, (c) Ag nanocube, and Ag nanocube@SiO_2, (d) Au nanocage@SiO_2, (e) Au nanocage (the upper) Au nanocage@SiO_2 (the lower) prepared with the addition of different volumes of 0.1-mM $HAuCl_4$ (aq) solution. (f) The photoluminescence spectra of CdTeS QDs and Au nanocage@SiO_2@CdTeS QDs.

4. Conclusions

In this paper, we demonstrate a novel approach to the formation of Au nanocage@SiO_2. Au nanocage@SiO_2@QDs multifunctional nanocomposites are expected to serve as optothermal-fluorescence nanoprobes for targeted mark and treatment. In the process of boiling water etching, the inner SiO_2 is preferentially etched. The yolk-shell structure of Au nanocage@SiO_2 is synthesized. This structure can be further explored as a drug carrier.

References

[1] Sun Y G and Xia Y N 2004 *J. Am. Chem. Soc.* **126** 3892
[2] Skrabalak S E, Au L, Li X D and Xia Y N 2007 *Nat. Protoc.* **2** 2183
[3] Chen J, Sun Y G, Lu X M, Au L, Cobley C M and Xia Y N 2008 *Acc. Chem. Res.* **41** 1587
[4] Young J K, Figueroa E R and Drezek R A 2012 *Ann. Biomed. Eng.* **40** 438
[5] Yavuz M S, Cheng Y Y, Chen J Y, Cobley C M, Zhang Q, Rycenga M, Xie J W, Kim C, Song K H, Schwartz A G, Wang L V and Xia Y N 2009 *Nat. Mater.* **8** 935
[6] Yang X M, Skrabalak S, Stein E, Wu B, Wei X B, Xia Y N and Wang L V 2008 *Proc. SPIE* **6856** 68560I
[7] Kong X M, Yu Q, Zhang X F, Du X Z, Gong H and Jiang H 2012 *J. Mater. Chem.* **22** 7767
[8] Bahadur N M, Watanabe S, Furusawa T, Sato M, Kurayama F, Siddiquey I A, Kobayashi Y and Suzuki N 2011 *Elsevier B.V.* **392** 137
[9] Li C Y, Zhu Y H, Zhang X Q, Yang X L and Li C Z 2012 *RSC Adv.* **2** 1765
[10] Zhou F, Liu Y and Li Z Y 2011 *Chin. Phys. B* **20** 037303
[11] Gao F, Han J X, Lü C F, Wang Q, Zhang J, Li Q, Bao L R and Li X J 2012 *Nanopart. Res.* **14** 1191
[12] Mathias S, Christian C, Philip B, Eoin M and Tobias K 2011 *Langmuir* **27** 727
[13] Guo L Q, Guan A H, Lin X L, Zhang C L and Chen G N 2010 *Talanta* **82** 1696
[14] Khlebtsov B, Panfilova E, Khanadeev V, Bibikova O, Terentyuk G, Ivanov A, Rumyantseva V, Shilov I, Ryabova A, Loshchenov V and Khlebtsov N G 2011 *ACS Nano.* **27** 7077
[15] Zhang R C, Liu L and Xu X L 2011 *Chin. Phys. B* **20** 086101
[16] Yin N Q, Liu L, Lei J M, Liu Y S, Gong M G, Wu Y Z, Zhu L X and Xu X L 2012 *Chin. Phys. B* **21** 116101
[17] Siekkinen A R, McLellan J M, Chen J Y and Xia Y N 2006 *Chem. Phys. Lett.* **432** 491
[18] Chen J Y, McLellan J M, Siekkinen A, Xiong Y J, Li Z Y and Xia Y N 2006 *J. Am. Chem. Soc.* **128** 14776
[19] Li L L, Zhang Y Q, Hao N J, Chen D and Tang F Q 2012 *Chin. Sci. Bull.* **57** 36313638
[20] Wong Y J, Zhu L F, Teo W S, Tan Y W, Yang Y H, Wang C and Chen H Y 2011 *J. Am. Chem. Soc.* **133** 11422
[21] Mao W Y, Guo J, Yang W L, Wang C C, He J and Chen J Y 2007 *Nanotechnology* **18** 485611
[22] Liu N G, Prall B S and Klimov V I 2006 *J. Am. Chem. Soc.* **128** 15362
[23] Ung T, Liz-Marzán L M and Mulvaney P 1998 *Langmuir* **14** 3741
[24] Hermoso W, Alves T V, Ornellas F R and Camargo P H C 2012 *Eur. Phys. J. D* **66** 135
[25] Kan C X, Zhu J J and Zhu X G 2008 *J. Phys. D: Appl. Phys.* **41** 155304
[26] Ringe E, McMahon J M, Sohn K, Cobley C, Xia Y N, Huang J X, Schatz G C, Marks L D and Van Duyne R P 2010 *J. Phys. Chem. C* **114** 12513