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Surfactant-regulated fabrication of gold nanostars in magnetic core/shell hybrid nanoparticles for controlled release of drug

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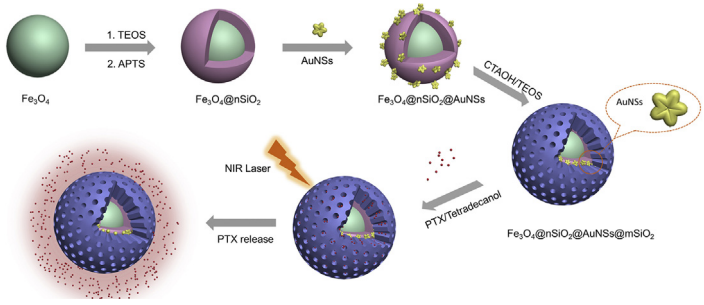
GRAPHICAL ABSTRACT



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ABSTRACT

Core-shell nanostructured materials, which are of great interest for fundamental research and industrial applications, have properties that can be enhanced by combining component superstructures. Here, we report the new construction of magnetic core-shell gold nanostars (AuNSs) for controlled release of drug. The AuNSs were successfully embedded intact between an inner silica layer and outside mesoporous silica layer to create magnetic core/shell hybrid nanoparticles by using a base cationic templating surfactant, cetyltrimethylammonium hydroxide (CTAOH). The core-shell nano-composites containing AuNSs exhibit the characteristics including high magnetization, mesoporous nanostructure, photothermal properties and low in vitro toxicity, showing the potential applications for drug delivery and controlled release.

1. Introduction

In the past decades, superparamagnetic nanoparticles have been extensively pursued for bioseparation [1,2], biosensor [3], drug delivery [4] and magnetic resonance imaging [5,6] applications because of their numerous advantages, biodegradation and potential to be non-cytotoxic to humans [7–9]. At present, iron oxide nanocrystals with precisely controlled size distribution have been prepared via many approaches [10–13], and the most common composites of multifunctional magnetite nanoparticles are core/shell structures coupled with other functional materials. This kind of nanoarchitecture usually consists of a magnetic core surrounded by a functional shell composed of polymer molecules [14], metal nanomaterials [3,15–17], carbon [18], or silica materials [19], which should extend their applications. Magnetic nanocomposites with mesoporous shells are ideal candidates for adsorption, separation, sensing and drug carrier applications due to their stable mesoporous structure, accessible pore size, and high specific surface area [4,6,20–22]. Gold nanoparticles (AuNPs) with numerous morphologies such as sphere, rod, cube, shell, disk, and star are equally attractive in many fields [23,24]. Mesoporous

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magnetic nanocomposites combined with AuNPs are interesting and promising for researchers. Gold nanoshells, nanospheres and nanorods modified with mesoporous silica layers have been investigated [22,25,26]. In general, the preparation of the plasmonic gold nanomaterials such as nanoshells, nanocages and nanorods are very complicated. However, the preparation of AuNSs is more simple which only needs to mixture of the solution of reductant and chloroauric acid. Besides, AuNSs also have many excellent properties, e.g., thermal characteristics and controllable size. Even though much attention has been given to photodynamic therapy with AuNSs [27–30], studies about AuNSs modified with materials such as porous silicon to make complex nanoparticles still remains a great blank. One main reason is likely the instability of AuNSs throughout the modification process, especially throughout the process of building mesoporous silica layers. The branched structure of AuNSs is extremely sensitive to nanoparticle modification reaction conditions as well as conditions required for removal of templates, which greatly limits the applications of AuNSs in many fields.

Herein, the AuNSs were introduced intact into the core-shell microspheres using a modified surfactant-templating approach. The obtained microspheres not only possess superparamagnetism, high surface area, and ordered mesopores, but also photothermal properties by means of the AuNSs. The AuNSs were immobilized between the mesoporous silica shells and magnetic cores without destroying the star structures using CTAOH as a soft template. The synthesis process is presented in Scheme 1. The Fe_3O_4 cores were synthesized via a hydrothermal method. The Fe_3O_4 cores were coated (@) with silica shells ($nSiO_2$) though a sol-gel process using ethylsilicate (TEOS) to form the hybrid nanoparticles designated Fe_3O_4@$nSiO_2$. And then (3-aminopropyl) triethoxysilane (APTS) formed a uniform silica layer capped with abundant amino groups to which the AuNPs could attach through coordination bonds [22,31]. After that, AuNSs were attached to the amino groups of the Fe_3O_4@$nSiO_2$ through incubation in solution and coated on the surface of Fe_3O_4@$nSiO_2$ to form the Fe_3O_4@$nSiO_2$@AuNSs nanoparticles. Subsequently, the outer mesoporous silica layers (designated $mSiO_2$) of Fe_3O_4@$nSiO_2$@AuNSs were formed using cationic CTAOH as the templating agent and TEOS as the silica source to form Fe_3O_4@$nSiO_2$@AuNSs@$mSiO_2$ for drug carriers.

The photothermal effect of Fe_3O_4@$nSiO_2$@AuNSs@$mSiO_2$ nanocomposites upon near-infrared (NIR) irradiation can increase the local temperature to induce a phase transition in tetradecanol allowing tetradecanol to act as a temperature-sensitive gatekeeper of nanoparticle-loaded drugs. As a result, upon NIR irradiation, the drug can be released from Fe_3O_4@$nSiO_2$@AuNSs@$mSiO_2$ nanoparticles. Since NIR irradiation and photo-thermal treatment can not only affect the cancer cells but also have an unavoidable effect on the normal cells. In this work, the hybrid nanoparticles can be controlled targeted because of the magnetic Fe_3O_4 as the inner core. Thereby the magnetic field can be used to control the distribution of nanoparticles and then the local NIR irradiation would reduce the damage to normal cells. When being applied to deliver paclitaxel (PTX) via photothermal therapy, the synthesized nanocomposites exhibit a favorable controlled release effect due to the photothermal property of AuNSs. When tetradecanol is introduced as thermo-sensitive medium in order to realize drug loading, the complex nanoparticles can control the release of drugs by inducing the phase transition of tetradecanol which extend the applications of AuNSs within nanocomposites.

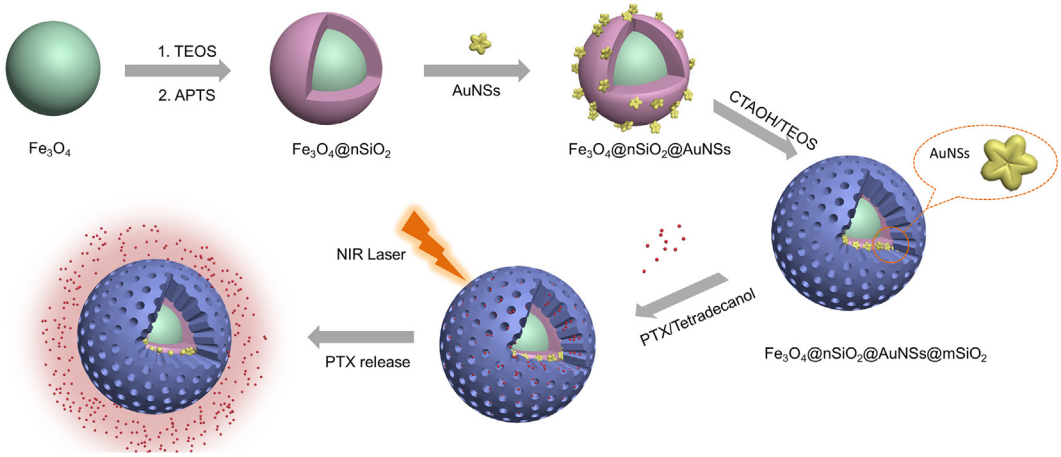
2. Experimental section

2.1. Chemicals and materials

Ethylene glycol, NaOH (purity > 97%), $FeCl_3{\cdot}6H_2O$ (purity > 99%), Tween 80, and sodium acetate (purity > 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Poly(4-styrenesulfonic acid-*co*-maleic acid) sodium salt (PSSMA, $n_{4\text{-styrenesulfonic acid}}:n_{\text{maleic acid}} = 1:1$) was purchased from Aladdin Industrial Corporation (Shanghai, China). Cetyltrimethylammonium bromide (CTAB, purity 100%), TEOS, APTS (purity > 98%), 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES, purity > 99%), tetradecanol (purity > 99%), PTX (purity > 98%), and gold (III) chloride trihydrate ($HAuCl_4$, 49.0% Au) were obtained from J&K Chemical Company, Ltd. (China). All chemicals were used without further purification. The water used in the experiments was obtained using a UPH-IV ultrapure water apparatus (China) with a resistivity of 18.25 MΩ·cm.

2.2. Synthesis of multicomponent Fe_3O_4@$nSiO_2$@AuNSs@$mSiO_2$

Synthesis of Fe_3O_4 Nanoparticles. The Fe_3O_4 nanoparticles were synthesized by means of a solvothermal reaction [32]. Briefly, 1.13 g of $FeCl_3{\cdot}6H_2O$ was dissolved in 70 mL of ethylene glycol under magnetic stirring for 30 min to form a homogeneous solution, followed by the addition of PSSMA (1.75 g) and sodium acetate (5.25 g). The obtained red-brown solution was then sealed in Teflon-lined stainless-steel autoclave and heated at 200 °C for 12 h. The autoclave was cooled to room temperature. The obtained



Scheme 1. Formation process of Fe_3O_4@$nSiO_2$@AuNSs@$mSiO_2$ nanocomposites.