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Article

Chemistry

Fabrication of superstable gold nanorod–carbon nanocapsule as a molecule loading material

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Abstract In this work, we fabricated a monodisperse nanocomposite by coating gold nanorods (AuNRs) with a layer of biocompatible, stable carbon, obtaining AuNR@Carbon core–shell nanocapsules, which without any functionalization could be used as a molecule loading material due to its high surface areas. In this system, the AuNR core had a high-absorption cross section for conversion of near-infrared light to heat, which could be explored for local hyperthermia. The carbon shell, which was biocompatible and stable even under concentrated acidic and alkaline conditions, was able to adsorb molecules with π–π interactions or electrostatic interactions. In comparison with AuNR@SiO_2, AuNR@Carbon nanocapsules demonstrate the following merits: (1) simple and green synthesis method, (2) far more stable with respect to high-temperature stability and (3) larger molecule loading capacity, which indicate great potential in the biomedical applications.

Keywords AuNR@Carbon nanocapsules · AuNR@SiO_2 nanocapsules · Stability · Adsorption capacity

1 Introduction

In recent years, noble metal nanoparticles, especially gold nanoparticles, have caused widespread concern due to their remarkable optical, thermal and electrical properties. Different gold nanoparticles have been successfully synthesized to study their corresponding optical properties [1]. In these gold nanoparticles, gold nanorods (AuNRs) have proven to be promising in a wide range of biomedical applications and ideally suited for theranostic and thermo-chemotherapeutic applications, owing to their tunable localized surface plasmon resonance (LSPR) and photothermal effects [2–5].

However, AuNRs as NIR-absorbing inorganic nanomaterials, although having shown great promise not only to photothermally kill cancer cells but also to enhance the efficacy of other types of therapies, were not stable and would be aggregated without surfactants such as hexadecyl trimethyl ammonium bromide (CTAB) in a short time. To reduce often observed clustering and aggregating of the AuNRs without CTAB, the surface of AuNRs is often modified with mesoporous silica or all kinds of polymers [6, 7]. And the large specific surface area of mesoporous silica and polymers guarantees the large loading capacity [8–10]. Nevertheless, the performance of these modified nanocapsules is not as good as initially envisioned. First, the mesoporous silica or polymers cannot withstand high temperature, and mesoporous silica or polymers usually will come away from the AuNRs during the laser

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irradiation [11, 12]. Second, the organic solvents, initiators or toxic reagents are commonly used during the synthetic procedure of polymer or silica shell [13], which will be harmful and toxic. Third, the molecule loading capacity of AuNR@Polymer or AuNR@SiO_2 is limited.

In order to overcome the above shortcomings, we herein reported the synthesis of a novel type of stable, biocompatible AuNR@Carbon core–shell nanocapsules, by an in situ coating method. Monodispersed AuNR@carbon core–shell nanocapsules were prepared by a hydrothermal treatment in aqueous glucose solutions (AuNR@Carbon, Fig. 1) [14–17].

2 Materials and methods

2.1 Materials

CTAB and L-ascorbic acid (AA) were purchased from Sigma. Anhydrous chloroauric acid ($HAuCl_4$), glucose, tetraethyl orthosilicate (TEOS) and methylene blue (MB) were purchased from Aladdin. All other chemical reagents were analytical grade and used without further purification. The ultrapure water was from Milli-Q Integral System. Other chemicals were all commercially available.

2.2 Synthesis of AuNR nanoparticles

AuNRs with a large average aspect ratio were prepared following a seed-mediated growth method. An aqueous mixture solution of $HAuCl_4$ (0.01 mol/L, 0.25 mL) and CTAB (0.1 mol/L, 9.75 mL) was added into a freshly prepared, ice-cold aqueous $NaBH_4$ solution (0.01 mol/L, 0.6 mL) as the seed solution. The resultant solution was mixed by rapid stirring with magnetic stirrers and then kept at room temperature for 2 h before use. The growth solution was prepared by mixing together $HAuCl_4$ (0.01 mol/L, 20 mL), $AgNO_3$ (0.01 mol/L, 4 mL) and CTAB (0.1 mol/L, 400 mL) and then adding a freshly prepared aqueous ascorbic acid solution (0.1 mol/L, 3.2 mL) and an aqueous HCl solution (1.0 mol/L, 8 mL). After the resultant solution was mixed by inversion, the seed solution (1 mL) was rapidly injected. The reaction mixture was subjected to gentle inversion for 10 s and then left undisturbed for at least 6 h.

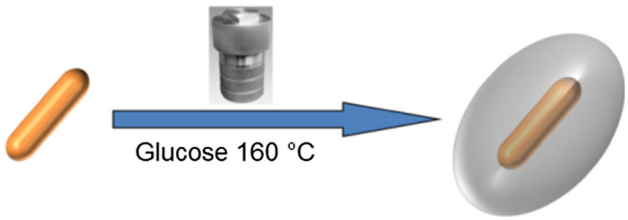

Fig. 1 (Color online) Schematic illustration of AuNR@Carbon nanocapsule fabrication

2.3 Synthesis of AuNR@Carbon nanocapsules

AuNR@Carbon nanocapsules were fabricated through the hydrothermal method. A 55 mL of the produced AuNRs was centrifuged and washed with double-distilled water to remove excess CTAB surfactant and then dispersed in 12 mL of double-distilled water with vigorous magnetic stirring to form a dark solution. Following this step, 0.6 g glucose was added into the previous solution, and the mixture was stirred for 15 min. The final solution was transferred to a Teflon-lined stainless steel autoclave (15 mL in total volume), sealed and maintained at 160 °C for 12 h. The final product was centrifuged and washed with double-distilled water several times until the supernatant was colorless.

2.4 Synthesis of AuNR@SiO_2 nanocapsules

A 15 mL of produced AuNRs was centrifuged and washed with double-distilled water at 10,000 r/min for 30 min to remove excess CTAB surfactant, followed by dispersal in 10 mL of double-distilled water. One hundred microliters of 0.1 mol/L NaOH solution was added upon stirring. Then, three 6 μL injections of pure TEOS were added under gentle stirring at 30-min intervals. The reaction mixture was reacted for 3 days.

2.5 Characterizations

Transmission electron microscopy (TEM) images were obtained by JEM-2010 (JEOL). Scanning electron microscopy (SEM) imaging of AuNR@carbons was tested by field emission electron microscopy (Tecnai G2F20 S-TWIN). The UV–Vis spectra were measured on the UV-2450 spectrophotometer (Shimadzu). The FTIR spectra were measured by Nicolet 5700 (Thermo Nicolet). The hydrodynamic diameters were measured using a Zetasizer Nano ZS90 DLS system (Malvern Instruments Ltd.), and ζ-potential measurements were carried out at room temperature on the Zetasizer Nano ZS90 Zeta system (Malvern Instruments Ltd.).

3 Results and discussion

3.1 Structural characterization of AuNR@Carbon nanocapsules

AuNRs with a relatively large average aspect ratio of 3.5–4.0 were fabricated according to a seed-mediated growth