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Synthesis of gold-spikes decorated biomimetic silica microrod for photothermal agents

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ABSTRACT

Photo-absorbing molecules or nanoparticles as microscopic heat sources are expected to improve the therapeutic accuracy and reduce side effect on normal tissues. Herein, gold (Au)-spikes decorated silica structure based on a unicellular organism (*Escherichia coli*) as a framework was synthesized using E@SiO_2-Au spikes as the reusable photothermal agents. The synthesized E@SiO_2-Au spikes were stable under the irradiation of 808 nm NIR laser after 5 times recycling experiments, with no temperature decrease tendencies. As a result of temperature evaluation measurements, E@SiO_2-Au spikes showed better performance with higher conversion efficiency and more stable activity during multiple reaction runs.

Introduction

There have been significant efforts in cancer treatment for the past several years, but the conventional approaches, drug therapies, cause considerable unintended damage to cell nearby. In contrast, photothermal therapy (PTT), which only uses the near-infrared (NIR) laser to target only the intended portion, causes negligible damages to surrounding tissues and cellular components [1,2]. PTT system passively increase tumor-accumulation via the enhanced penetration and retention effect [3]. Thus, PTT using functional nanoparticles as microscopic heat sources and photo-absorbing materials is expected to enhance the therapeutic accuracy and reduce side-effect on normal tissues [4].

Numerous efforts have been made toward the preparation of NIR-absorbing agents with strong NIR absorbance and high photothermal conversion [5–7]. Photo-absorbing agents under the irradiation of NIR laser induced electronic extinction in the form of electron–hole pairs, followed by scattering to yield a Fermi distribution elevates temperature [8]. Therefore, it is desirable to use photothermal agents with strong absorption in the NIR light (700–1000 nm), which can penetrate deeper through soft tissues with minimum absorption [9]. In addition, the conversion of lower-energy light into high energy emission in the NIR light-to-heat conversion process is critical for the successful ablation of target cells [5,8]. A variety of NIR-absorbing agents, such as gold nanoparticles, quantum dots, carbon nanotubes, and indocyanine green (ICG) have all been investigated and shown promise in diverse biomedical applications [9–12]. These anticancer nano-systems have already been approved for clinical use, due to their excellent treatment efficacy [13–15]. Among the photothermal agents, gold-based nanostructures with high efficiency of photo-thermal conversion, generation heat from absorbed NIR light, have been extensively explored [11]. It is easy to adjust the optical properties of gold nanostructures by controlling structural dimensions [12], increasing their photothermal conversion efficiency.

Herein, the gold-spikes decorated silica structure based on a unicellular organism, *Escherichia coli* (*E. coli*), as a framework was synthesized. Gold-spikes were utilized in the design of high-performance photothermal conversion and showed highly absorbing NIR [16–19]. Temperature monitoring of aqueous samples was estimated in real time, and a temperature increase at 59 °C was recorded. In the case of tumor tissues, local hyperthermia at temperatures above 45 °C has been shown to directly trigger cancer cell death [1,12]. Therefore, E@SiO_2-Au spikes prepared herein were sufficient to apply in PTT. To reveal the nature of such excellent photothermal effects, photothermal conversion efficiency (η) was measured [17–22].

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Experimental

In vitro E. coli *growth*

E. coli strains were cultured in Luria–Bertani medium for the use of framework. Yeast extracts (0.5 g), sodium chloride (1 g), and tryptone (1 g) were resolved in 100 mL DI water. The *E. coli* dispersed medium was incubated at 37 °C for 48 h with shaking at 180 rpm. The cell dry weight was 66.9 ± 7.21 mg. The cell culture medium was centrifuged three times with DI water and re-dispersed in 15 mL DI water. After that 10 mL of re-dispersed *E. coli* solution was injected into the new-culturing medium for further incubation, and the extra solution that was not re-dispersed was dispersed in 20% DI water and 80% ethanol solution for silica layer coating.

Synthesis of E@SiO$_2$

The E@SiO$_2$ sample was prepared by coating the *E. coli* with SiO$_2$. Coating of *E. coli* with a SiO$_2$ layer was carried out by the modified Stober method [22–25]. The *E. coli* was dispersed in a mixture of 80 v/v% ethanol and 20 v/v% water, followed by sequentially adding NH_4OH and tetraethyl orthosilicate (TEOS) solution dropwise. The mixture was stirred for 6 h, and the resulting E@SiO$_2$ particles were separated, collected by centrifugation, and washed with ethanol three times. Finally, the particles were re-dispersed in ethanol and dried for further use.

Preparation of Au spikes

For preparation of Au spikes, Ag NPs were prepared as reported previously. In brief, the method is as follows: 0.0425 g/10 mL solution was added to boiling 80 mL DI water, followed by adding 1 wt% trisodium citrate dihydrate (TSC) solution. The solution was boiled for 20 min and cooled down to room temperature. The color of the solution turned pale yellow to green. Au spikes were synthesized as follows: 5 mL the prepared Ag NPs was dispersed in 3 mM $HAuCl_4$ 25 mL and injected into ascorbic acid (AA) solution (10 mM, 5 mL). The color of the solution turned green to blue immediately. Polyvinylpyrrolidone (PVP, 0.1 g/mL) was added in the solution at 50 °C for 6 h.

Synthesis of E@SiO$_2$-Au spikes

In order to decorate Au spikes on the surface of E@SiO$_2$, an amine functional group was introduced. (3-Aminopropyl)triethoxysilane (APTES) was slowly added to the 40 mL ethanol solution of 0.01 g E@SiO$_2$, and the mixture was stirred at 50 °C for 12 h to ensure complete functionalization. The precipitated particles were separated by centrifugation, washed thrice with ethanol, and re-dispersed in water. The APTES-functionalized E@SiO$_2$ solution (20 mL) was then added to the PVP-coated Au spikes NP solution (700 mL). After 6 h, the resulting particles were collected by centrifugation and washed 3 times with water to obtain E@SiO$_2$-Au spikes particles.

Characterization and photothermal performance

The particles morphology and dispersion were investigated by transmission electron microscopy (TEM, JEOL JEM-2010) and scanning electron microscopy (SEM, SEC SNE-3000 M). Their UV–vis absorption spectra were measured using a spectrophotometer (UV-1800, Shimazdu). The photothermal performance was investigated using 808 nm NIR pulsed laser (4 W/cm^2). The distance between the sample and the light source was set to 10 cm to adjust the photo-intensity (200 lx). The solution containing

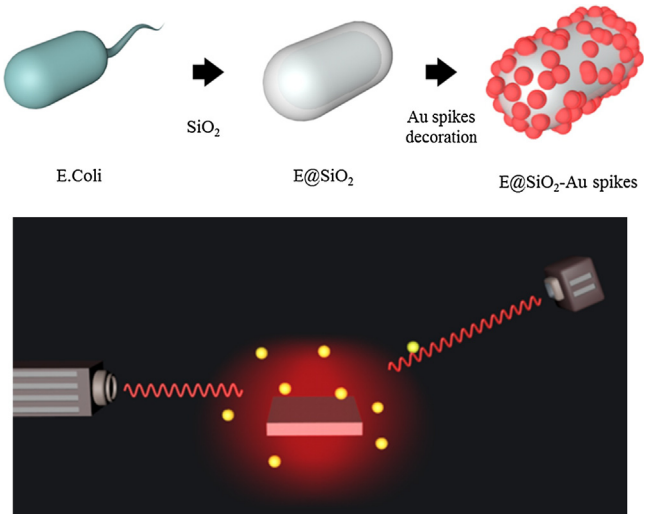

Fig. 1. Schematic illustration of synthetic procedures of E@SiO$_2$-Au spikes nanostructure and optical layout of laser setup for measurement of photothermal performance.

300 μg/mL and E@SiO$_2$-Au spikes was placed in a quartz cuvette. The laser was pulsed into the solutions for 10 min and turned off. During which, the reaction temperature was measured using a NIR camera (CompactXR, seekthermal)

Results and discussion

Characterization of E@SiO$_2$-Au spikes

For the synergistic combination of PTT, Au spikes were fabricated onto the silica coated *E. coli* as shown in Fig. 1. The separated *E. coli* sample worked as the framework for the support of Au spikes. Unicellular cells, especially *E. coli*, were easily cultivated and reproduced. Thus, using them as frameworks was an adequate strategy for easy modification. *E. coli* were dispersed for at least 12 h in 80 v/v% ethanol solution for silica coating.

To prepare E@SiO$_2$-Au spikes, Au spikes were synthesized as reported previously. Au spikes made from Ag NPs after the modification via the galvanic reaction. TSC and AA were used as stabilizer and reduction agent of gold ions, respectively. Prior to the

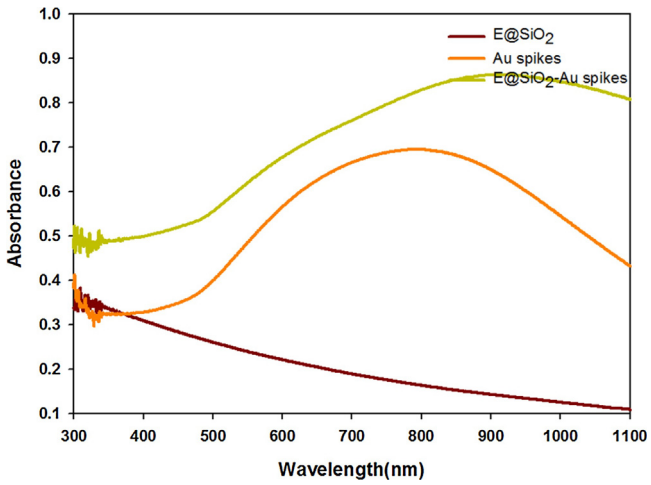

Fig. 2. UV–vis spectrometer of E@SiO$_2$, Au spikes and E@SiO$_2$-Au spikes nanostructures.