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Photothermal lysis of pathogenic bacteria by platinum nanodots decorated gold nanorods under near infrared irradiation

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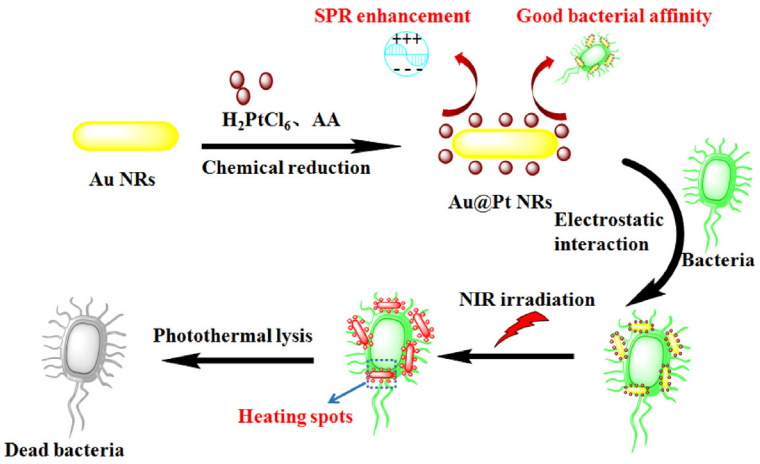
HIGHLIGHTS

- Photothermal lysis is a good method for killing bacteria in the environment.
- Au@Pt NRs were composed by single crystalline Pt nanodots covered on Au NRs.
- The photothermal efficiency of Au@Pt NRs can be tuned by the Pt nanodot loading.
- Au@Pt NRs facilitated the interaction with bacteria due to the Pt decoration.
- Au@Pt NRs present a good effect on killing bacteria, as compared to Au NRs.

GRAPHICAL ABSTRACT

Bimetallic Au@Pt nanorods showed enhancement in bacterial affinity and photothermal bactericidal efficiency under NIR irradiation.



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ABSTRACT

Photothermal lysis is an effective method for fast removal of pathogenic bacteria from bacterial contaminated environments and human body, irrespective of bacterial drug resistance. In the present work, a highly effective photothermal agent, Au@Pt nanorods (NRs), was prepared by modification of Pt nanodots with particle size of 5 nm on the surface of Au NRs with a length of *ca.* 41 nm and a width of *ca.* 13 nm. The LSPR absorbance band of Au@Pt NRs could be tuned from 755 to 845 nm by changing the Pt loading from 0.05 to 0.2, as compared to Au NRs. The photothermal conversion efficiency of Au@Pt NRs depended on the Pt loading, Au@Pt NRs concentration, and power density. Under NIR irradiation, the $Au@Pt_{0.1}$ NRs exhibited the highest efficiency in photothermal lysis of both gram-positive and gram-negative bacteria. The introduction of Pt nanodots on the surface of Au@Pt NRs not only enhanced their photothermal conversions but also enhanced their affinity to bacteria and significantly decreased their cytotoxicity. The photothermal lysis of bacteria over Au@Pt NRs caused the damage onto the cell walls of bacteria, implying that the killing of bacteria probably went through the thermal ablation mechanism.

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1. Introduction

Only a few of bacteria can contaminate food, drinking water, medical equipment or any other environment due to their high reproductive rate, which possibly leads to some serious infections for human being. The use of antibiotics is a common effective way for the removal of bacteria. However, the overuse of antibiotics causes the emergence of multidrug resistant bacteria, becoming a great threat to the health of human [1]. Recently, great effort has focus on the development of new methods, such as novel antibacterial material [2], antimicrobial photodynamic therapy [3], and photothermal lysis [1,4], to deal with this problem. From among them, photothermal lysis emerged as an approach that can convert the light into heat with photothermal agent, which relies on the use of hyperthermia to kill the bacteria, irrespective of their drug resistance [5]. In the photothermal therapy process, the photothemal agent plays the main role. Therefore, much attention has been paid on the research and development of novel photothermal nanoagents with high light and heat conversion efficiency, good bacterial affinity, and low cytotoxicity [6–11].

In recent years, gold nanomaterials have attracted much attention in biomedical applications, such as optical sensing [12], optical imaging [13], diagnostics [14], drug delivery [15], and cancer therapy [5,16] because of their unique optical properties and good bioinert. In particular, due to the localized surface Plasmon resonance (LSPR), the gold nanomaterials have become excellent candidates for photothermal therapy (PTT). The morphology of gold nanoparticles significantly affects their light and heat conversion efficiency. For example, gold nanoparticles with shapes of nanospheres, nanorods, nanoshells, nanocages and nanostars have been used in PTT [17–21]. As compared to other nanostructures, gold nanorods (Au NRs) can absorb laser light wavelength in the near infrared (NIR) region, which is a transparency window for biological tissues, and could efficiently transfer the absorbed NIR optical energy into heat [22]. The Au NRs based photothermal agents have attracted much attention in photothermal cancer therapy and bactericidal application [5,23–25].

In order to fast kill pathogenic bacteria, it is of great importance to improve the photothermal conversion efficiency of photothermal agent under NIR irradiation and enhance the interaction between photothermal agent and bacteria [3,26–29]. Towards nanorod-structural gold, increasing its aspect ratio is a comment and effective method to enhance its absorbance band in NIR region [6,18], which, however, is hard to be controlled due to the complex synthesis conditions and is difficult to remove the toxic surfactant, cetyltrimethylammonium bromide (CTAB) [30]. Recently, it has been reported that by modification of Pt or Pd nanodots on the surface of gold nanorods can controllably shift the absorbance band of gold nanorod from visible to NIR region [5,31,32]. Tang et al. [5] synthesized Au@Pt nanostructures with Au nanorods coated with a shell of Pt nanodots, showing promises in cancer photothermal therapy under NIR irradiation. Moreover, Pt nanoparticles with particle size of 5 nm were formed and located in the periplasm and on the cell wall of bacteria when $PtCl_6^{2-}$ ions were reduced by bacterium *Shewanella algae* [33,34], revealing that the Pt nanoparticles showed good affinity to bacteria. The Pt nanoparticles with particle size larger than 4 nm are also reported to be bacterio-compatible and less cytotoxic [35,36]. Thus, it is believed that decorating Pt nanoparticles on Au NRs is a feasible way to not only improve the photothermal conversion but also enhance the bacterial affinity and decrease the cytotoxicity in Au NRs based photothermal lysis of bacteria. Furthermore, to our best knowledge, it have not been reported for the application of Au@Pt nanostructures in photothermal lysis of pathogenic bacteria, the effect of Pt loading on the photothermal conversion efficiency, and the bacterial affinity of Au@Pt nanostructures.

Hence, in the present work, as shown in Scheme 1, bimetallic Au@Pt nanorods (NRs) with different Pt loading were prepared by modification of Pt nanodots on the surface of Au nanorods *via* wet chemical reduction method. The Au@Pt NRs had better photothermal conversion efficiency than the original Au NRs, and showed high photothermal bactericidal efficiency and good bacterial affinity in killing *Staphylococcus aureus* (*S. aureus*) and *Pseudomonas aeruginosa* (*P. aeruginosa*). The interaction between Au@Pt NRs and bacteria was discussed. A bactericidal mechanism for photothermal lysis of bacteria over Au@Pt NRs was proposed. Finally, the cytotoxicity of the original Au NRs and Au@Pt NRs was also investigated.

2. Experimental

2.1. Materials

Chloroauric acid ($HAuCl_4{\cdot}3H_2O$), hexachloroplatinic (IV) acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$), sodium borohydride ($NaBH_4$), L-ascorbic acid (AA) were purchased from Sinopharm Chemical Reagent Co., Ltd; cetyltrimethylammonium bromide (CTAB) was purchased from Shanghai Richjoint Chemical Reagent Co., Ltd; silver nitrate ($AgNO_3$) was purchased from Tianjin Damao Chemical Reagent Factory and poly(styrenesulfonic acid) sodium salt (PSS) were purchased from Alfa Aesar. Milli-Q water (18 MU cm) was used for all solution preparations.

2.2. Preparation of Au NRs

The Au NRs were prepared *via* a seed-mediated growth procedure [37]. Typically, an Au seed solution is first prepared by the following method: 0.25 mL of an aqueous 0.01 M solution of $HAuCl_4{\cdot}3H_2O$ was added to 7.5 mL of a 0.1 M CTAB solution in a test tube. The solution was gently mixed by the inversion. The solution appeared bright brown-yellow in color. Then, 0.6 mL of an aqueous 0.01 M ice-cold $NaBH_4$ solution was added all at once, followed by rapid inversion mixing for 2 min. The seed solution is allowed to react at 30 °C for 2 h before use. Afterwards, a growth solution containing of CTAB (4.75 mL, 0.10 M), $HAuCl_4$ (0.20 mL, 0.01 M), $AgNO_3$ (0.03 mL, 0.01 M) and AA (0.032 mL, 0.10 M) is prepared and mixed with 0.01 mL of the Au seed solution, and the mixture is allowed to react at 30 °C for at least 3 h. The obtained Au NRs were purified by centrifugation (12000 rpm, 10 min) three times before use. The Au NRs concentration of the resulting Au NRs suspension was detected by ICP, which was about 78.8 μg mL^{-1}.

2.3. Preparation of Au@Pt NRs

The Au NRs suspension (1 mL) was mixed with 5 μL of 0.01 M H_2PtCl_6 solution, respectively. Then, a 6 μL of 0.1 M AA was added. The mixture was shaken vigorously and then placed in a 30 °C water bath for at least 3 h, and the $Au@Pt_{0.1}$ was formed. $Au@Pt_{0.05}$ and $Au@Pt_{0.2}$ was prepared by the same method with 2.5 μL and 10 μL of H_2PtCl_6 solution and 3 μL and 12 μL of AA, respectively. The ICP analysis suggested that the Pt was almost loaded on Au NRs.

2.4. Characterization of NRs

Transmission electron microscopy (TEM) images were performed on a microscopy (Tecnai 12) operated at an acceleration voltage of 120 KV. High resolution transmission electron microscopy (HRTEM) images were obtained on a microscopy (Tecnai G2 F30) operated at an acceleration voltage of 200 KV. The TEM samples were prepared by placing a drop (5 μL) of NRs suspension onto a copper grid coated with a layer of amorphous carbon for 5 min, and then the residues were removed. The average aspect ratios of NRs (100 particles) were measured from the TEM images and calculated by a weighted-average method according to the