



Surface plasmon resonance-enhanced photothermal nanosensor for sensitive and selective visual detection of 2,4,6-trinitrotoluene



Xilin Bai, Suying Xu, Gaofei Hu, Leyu Wang*

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Environmentally Harmful Chemical Analysis, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:

Received 26 February 2016

Received in revised form 14 June 2016

Accepted 15 June 2016

Available online 17 June 2016

Keywords:

Nanosensor

Explosives detection

Visualized sensing

Surface plasmon resonance (SPR)

ABSTRACT

The exploration of feasible, reliable sensors for the selective and sensitive detection of nitroaromatic explosives is a critical issue nowadays as mandated by homeland security concerns. Our endeavor is to develop an instant on-site visual and ultra-sensitive photothermal nanosensor for 2,4,6-trinitrotoluene (TNT) detection, which could be applied on a broad scale with high selectivity and sensitivity. The fundamental principle of our work is that TNT could effectively induce the aggregation of the cysteamine-stabilized gold nanoparticles (Au NPs) by forming the Meisenheimer complex, which further enhanced the surface plasmon resonance (SPR) properties and the photothermal effects of Au NPs. Other coexisting nitroaromatics have negligible influences on the photothermal responses. By means of the temperature enhancement and photothermal imaging technique, the presence of TNT could be readily recognized and visualized, indicating wide potential applications in analytical sensing.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

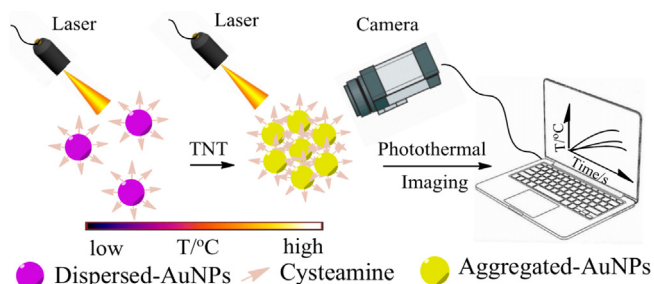
Rapid, sensitive and selective detection of nitroaromatic explosives such as 2,4,6-trinitrotoluene (TNT) is always desirable due to their great threat to the global security and human health [1–6]. To date, various methods have been developed for selective recognition of nitroaromatics, of which the optical sensing strategy holds great potentials in fabricating ultra-high sensitive probes. Taking advantages of nanotechnology, the development of nanomaterials with unique luminescent properties, such as semiconductor quantum dots (QDs) [5,7–11], lanthanide-doped nanocrystals [12–16], noble metal and carbon-based nanomaterials [17,18], organic dye-based nanomaterials [19,20] and metal-organic frameworks (MOFs) [21], has opened up new horizon for detection of nitroaromatics [22]. Yet, it is still intriguing to exploit a facial and versatile nanoplatform for the rapid and selective detection of TNT. The surface plasmon resonance (SPR) nanostructures have been widely investigated for enhanced catalysis and tumor ablation [23–29]. SPR-enhanced luminescence has also drawn wide attention for sensitive detection of small molecules [15,30]. In addition, noble metal nanostructure based-SPR and surface-enhanced Raman scattering (SERS) [10,31] have been extensively explored for constructing

optical biosensors, especially for label-free assays [32–38]. Yet, direct employment of SPR spectroscopy could be problematic since only those analytes with high molecular weight could afford observable SPR shifts. Alternatively, the SPR responses induced by small molecules need to be either amplified through some strategies or transformed into other types of signals that could be read out easily [39]. In recent decades, nanomaterials with photothermal effect have received wide attention for their applicability in photothermal therapy and photothermal imaging [29,40–45]. In particular, SPR-induced photothermal responses have gained substantial interests across various disciplines [44,46,47]. Notably, for the near-infrared light responsive photothermal agents, the consequent temperature changes are mainly originated from the photothermal effect of the photothermal agents, thus displaying low background signals from the external environment and possessing high sensing sensitivity.

Despite of the intrinsic high sensitive properties, the photothermal agents have rarely been utilized for sensing purposes. To date, our group has utilized the photothermal properties of polyaniline to successfully fabricate a photothermal sensor for selectively detection of nitroaromatics, which has demonstrated its great applicability [48]. The coinage metal-based nanostructures such as gold nanoparticles (AuNPs) are frequently utilized in designing sensors [49] owing to their localized SPR properties. Since the SPR changes of AuNPs arising from recognition event with analytes could also induce a color change, which has successfully been

* Corresponding author.

E-mail address: lywang@mail.buct.edu.cn (L. Wang).



Scheme 1. Schematic illustration of SPR-enhanced photothermal nanosensor based on TNT-induced aggregation of AuNPs.

utilized for constructing nitroaromatic sensors [18,50]. However, there is no platform that makes use of the SPR-enhanced photothermal effect of these nanomaterials for the highly selective and sensitive detection of TNT. Here, for the first time we explored the possibility of developing a photothermal nanosensor with superior selectivity and in situ detection of TNT under the assistance of SPR-enhanced photothermal effect.

In this work, the cysteamine-stabilized AuNPs were prepared, which were used to form the Meisenheimer complex with electron-deficient TNT through charge-transfer processes [10,12,22,48]. Such complexation further induces the aggregation of gold nanoparticles, resulting in a remarkable photothermal enhancement upon irradiation at 650 nm (Scheme 1). More importantly, the temperature of the Au NPs/TNT solution increases proportionally along with the increase of TNT concentration, which were scarcely affected by other nitroaromatics such as 2,4,6-trinitrophenol (TNP), 2,4-dinitrotoluene (DNT), nitrobenzene (NB), toluene (PhMe) and benzene (Ph). In addition, the temperature changes induced by TNT could also be visualized through photothermal imaging technique. Therefore, a novel SPR enhanced photothermal nanosensor for on-site visual and selective detection of TNT has been successfully developed.

2. Experimental

2.1. Reagents

2,4,6-Trinitrotoluene (TNT) and 2,4,6-trinitrophenol were supplied by the National Security Department of China and were recrystallized with ethanol before use. For safety considerations, all of the explosives must be kept away from fire, striking and friction, and they should be handled carefully. 2,4-Dinitrotoluene, nitrobenzene toluene and benzene were purchased from the Aladdin Chemistry Co. Ltd. These nitroaromatics were dissolved in mixed solvents of ethanol and acetonitrile (volume ratio of 4:1) to obtain the stock solution. In brief, 3.0 mg of each of nitroaromatics was dissolved in 15.0 mL of the mixture solvent containing ethanol (12.0 mL) and acetonitrile (3.0 mL) to get the stock solution with a final concentration of 0.2 mg/mL. All other reagents were analytical grade and used as received without further purification. Deionized (DI) water was used throughout. Cysteamine was purchased from Biological Science and Technology Co. Thiolated poly (ethylene glycol) (SH-mPEG, Mw = 5000) was purchased from Beijing Kaizheng Biological Engineering Development Co. Ethanol, acetonitrile, NaOH, NaHCO₃, Na₂CO₃, NaAc, HAc, Na₂HPO₄, NaH₂PO₄, NaF and HAuCl₄·2H₂O were received from Beijing Chemical Company (China).

2.2. Apparatus

The size and morphology of AuNPs were characterized by the H-800 transmission electron microscope (TEM). Dynamic

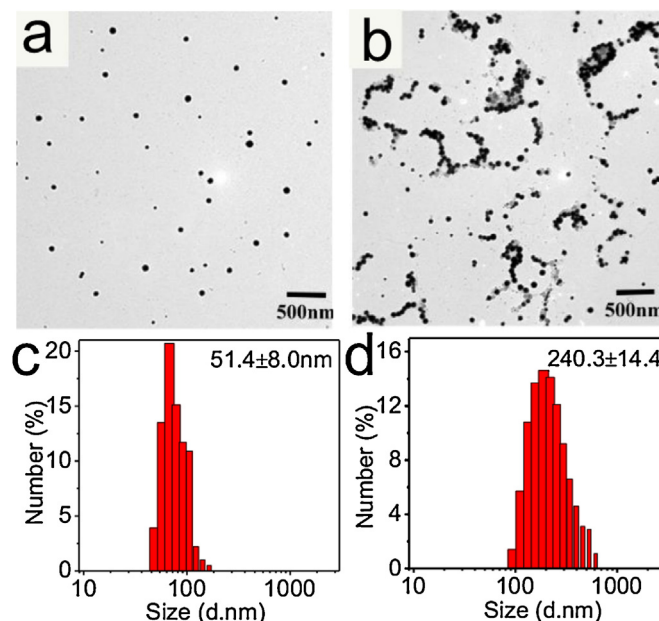


Fig. 1. TEM images (a, b) and DLS size distribution (c, d) of AuNPs-NH₂ before (a, c) and after (b, d) addition of TNT (4.0 μg/mL).

light scattering (DLS) particle size was measured by a Zetasizer Nano-ZS90 (Malvern) size analyzer. The absorption spectra were conducted on a Shimadzu UV-3600 spectrophotometer with a spectral window range of 200–3600 nm. The thermal imaging and temperature evolution plots were performed on a FLIR-A600 infrared (IR) camera.

2.3. Synthesis of amine-stabilized AuNPs

In brief, 1.0 mL of cysteamine (6.5 mM) was added to 40 mL of HAuCl₄ (2.0 mg) solution (100 °C) under magnetic stirring. Then 1.0 mg SH-mPEG was added to improve the stability of the as-synthesized Au NPs. The solution was kept boiling for 15 min till the solution turned into rose color. Finally, the NH₂ moiety functionalized hydrophilic gold nanoparticles (AuNPs-NH₂) were obtained after centrifugation and then redispersed into 3.0 mL of deionized water for later use.

2.4. Photothermal detection of TNT in solution

The amine-functionalized gold nanoparticles (AuNPs-NH₂) were obtained according to the previously published method [15]. Briefly, 50.0 μL of various concentrations of TNT or other nitroaromatics was mixed with 300 mL of the as-prepared AuNPs-NH₂. And then the mixed solution was diluted to 0.5 mL with NaH₂PO₄-Na₂HPO₄ (pH = 8.0, 20 mM) before being exposed to the laser irradiation. The photothermal tests were carried out with an IR camera to monitor and record the temperature changes while keeping the solution exposed to irradiation light at 650 nm with a power density of 2.25 W/cm².

3. Results and discussion

3.1. Morphology and photothermal properties of AuNPs-NH₂ NPs as photothermal nanosensors

In this study, cysteamine was used both as the electron donor to interact with electron-deficient nitroaromatics and surface ligands to stabilize the as-prepared AuNPs. As shown in Fig. 1a and c, initially, the AuNPs-NH₂ was well dispersed in deionized water

Download English Version:

<https://daneshyari.com/en/article/742250>

Download Persian Version:

<https://daneshyari.com/article/742250>

[Daneshyari.com](https://daneshyari.com)