



Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Seed-mediated growth of Au@Ag core-shell nanorods for the detection of ellagic acid in whitening cosmetics

Yi Wang^{a,*}, Yang Zeng^a, Wensheng Fu^a, Pu Zhang^{b,**}, Ling Li^a, Cuiying Ye^a, Lan Yu^a, Xiaochun Zhu^a, Song Zhao^a

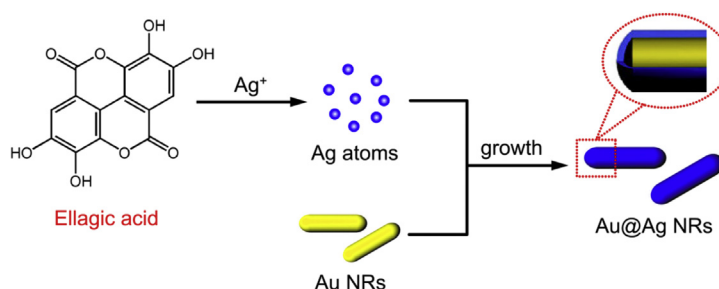
^a Chongqing Key Laboratory of Green Synthesis and Applications, College of Chemistry, Chongqing Normal University, Chongqing 401331, PR China

^b Research Center of Pharmacodynamics Evaluation Engineering Technology of Chongqing, College of Pharmacy, Chongqing Medical University, Chongqing 400016, PR China

HIGHLIGHTS

- Our sensor offers a simple solution for highly sensitive and selective detection of ellagic acid from realistic samples.
- Growth of Au@Ag core-shell nanorods from Au nanorods mediated by ellagic acid is applied to analytical chemistry.
- Sensing is based on monitoring of blue-shifts of the LSPR band accompanying formation of Au@Ag core-shell nanorods.
- This strategy can also be extended to other systems for antioxidant sensing.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 2 June 2017

Received in revised form

16 November 2017

Accepted 27 November 2017

Available online xxx

Keywords:

Gold nanorods

Seed-mediated growth

Surface plasmon resonance

Ellagic acid

ABSTRACT

Seed-mediated growth has been employed as a simple and powerful means to the shape-controlled synthesis of metal nanocrystals. In this work, we apply the principle of seed-mediated growth in analytical chemistry, and achieve improved sensitivity due to the low energy barrier in the target-induced formation of bimetallic nanoparticles with core-shell structure. As a result, a simple, reliable, highly sensitive and selective method for the detection of ellagic acid (EA), a naturally occurring polyphenolic antioxidant, has been developed. With the aid of EA in alkaline solution, Ag^+ ions can be transformed to Ag atoms and deposit on the surfaces of Au nanorods (AuNRs, act as seeds here) to generate Au@Ag core-shell nanorods, accompanied by blue shift of the longitudinal localized surface plasmon resonance (LSPR) band of AuNRs from near-infrared region to shorter wavelengths. Based on the linear relationship between the wavelength change of longitudinal LSPR band and the concentration of EA, our method achieves a detectable range of 0.2–20 μM and a limit of detection as low as 40 nM toward EA. This approach is highlighted by its high sensitivity for EA assay, which benefits from the viewpoint of thermodynamics in the nucleation/growth mode of metal nanoparticles. Moreover, this method shows high selectivity for EA detection when potential species coexist, and thus has been

* Corresponding author.

** Corresponding author.

E-mail addresses: ywang@cqu.edu.cn (Y. Wang), zhangpu51@hotmail.com (P. Zhang).

<https://doi.org/10.1016/j.aca.2017.11.067>

0003-2670/© 2017 Elsevier B.V. All rights reserved.

successfully applied in the detection of EA in skin-whitening cosmetics. The proposed strategy of seed-mediated growth herein can also be extended to other systems for sensing.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Antioxidants are the molecules that counteract free radicals and prevent the damage due to oxidants by crumbling them before they react with biological targets, preventing chain reactions or preventing the activation of oxygen to highly reactive products [1]. Ellagic acid (EA), one kind of naturally occurring polyphenolic antioxidants, can be found in a number of fruits like blackberry, blueberry, raspberry, grape, strawberry, and pomegranate [2]. Interest in EA has rapidly increased in recent years due to its beneficial health effects including antioxidant, antiviral, antimutagenic, and anticarcinogenic effects, as demonstrated by a large number of studies [3–6]. In skin-care or cosmetics industry, EA is one of the most popular ingredients in many kinds of cosmetic products (usually in the form of creams or lotions) because of its satisfactory skin-whitening effect, which is owing to the antioxidant activity of EA as well as its inhibition of tyrosinase activity and thus blocking the formation of melanin [7]. Analysis of EA content in commercial cosmetics is essential since its concentration has been strictly regulated. For instance, the content of EA is limited to 0.5% (w/w) for commercial cosmetics, which is declared by the Department of Health, Taiwan [8]. Therefore, developing convenient and reliable analytical methods for quantitative determination of EA would be useful in cosmetics industry. To our knowledge, methods including high performance liquid chromatography (HPLC) [9–13], spectrophotometry or ultraviolet (UV) spectrometry [12–14], resonance light scattering (RLS) technique [15], fluorescence spectrophotometry [16], voltammetry [8,17–19], and capillary electrophoresis (CE) [11] have been employed to determine EA. However, many of the available methods for EA detection are limited in practical applications owing to their intrinsic shortcomings of time-consuming, poor sensitivity, requiring expensive instruments and complicated sample preparation protocols. For instance, the detection of EA by spectrophotometry and UV spectrometry usually suffers from the interference by coexisting substances in the real-life samples since the absorption of EA is located at UV region. Thus, complex derivatizations of EA are needed to make the absorption peak red-shift to visible region and thus improve the selectivity of the analytical methods [14]. As to the commonly used reversed-phase HPLC method (with C_{18} column), the ionization of EA easily occurs in polar mobile phase, which significantly affects the chromatographic peak profile (e.g., peak tailing) and thus the calculation of peak area for quantitative analysis [9]. Therefore, it is imperative to develop simple, rapid, sensitive and selective analytical methods for EA assay.

Metal nanoparticles and their relevant composites with different architectures have been widely used as analytical probes for assay due to their remarkable optical and electric properties, especially localized surface plasmon resonance (LSPR) [20–23]. The composition, shape, size, and surface chemistry of a metal nanoparticle can be well tuned through the introduction of certain target molecules for obtaining different LSPR signal. Based on the LSPR variation of metal nanoparticles caused by the target molecules, a variety of different analytical methodologies and techniques can be developed. Gold nanorods (AuNRs) are nanometer-sized gold particles with a rod shape, whose LSPR can be readily tuned in the visible to near-infrared region by manipulating their

aspect ratios (i.e., length/diameter) during the synthesis. Owing to their unique structure and physical properties, AuNRs have attracted extensive attention in recent years in the fields of chemical sensing [24], biomedical imaging [25], photothermal therapy [26], photocatalysis [27], and solar cells [28].

In this work, using AuNRs as an optical probe, we develop a simple and sensitive method for the detection of EA based on seed-mediated growth of Au@Ag core-shell NRs. Seed-mediated growth, in which newly formed atoms are deposited onto the surfaces of preformed seeds via heterogeneous nucleation, has emerged as a simple and powerful means to the shape-controlled synthesis of metal nanocrystals [29–31]. Herein, we employ AuNRs as seeds and silver nitrate as Ag precursor. In the presence of EA (see molecular structure in Scheme 1), Ag atoms can be generated from the redox reaction between silver nitrate and EA, and then deposit on the surfaces of AuNRs via heterogeneous nucleation. As a result, a new structure with an AuNR core and a thin layer of Ag shell is obtained (Scheme 1), meanwhile, the LSPR peak of AuNRs continuously blue shift along with the increase of EA concentration. Based on the quantitative relationship between the wavelength change of LSPR peak and the concentration of EA in the system, a new analytical method for the detection of EA is established. According to the knowledge of thermodynamics, heterogeneous nucleation only needs to step over much lower energy barrier than the homogeneous nucleation when the formation of metal NPs [32,33]. Thus, only trace amount of reductant/antioxidant (e.g., EA in the present work) in the reaction system can achieve the transformation of Ag^+ into Ag atom and growth on the AuNR seeds, which could largely improve the sensitivity of the analytical methods for EA assay. In addition, this method shows satisfying selectivity toward EA and has been successfully applied in the detection of EA in commercial whitening cosmetics.

2. Experimental

2.1. Chemicals and materials

Silver nitrate ($AgNO_3$) and hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 3H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). L-ascorbic acid (AA), hexadecyltrimethylammonium bromide (CTAB), 5-bromosalicylic acid (5-BrSA), and sodium borohydride ($NaBH_4$) were purchased from Aladdin Industrial Corporation (Shanghai, China). Ellagic acid was obtained from Xiya Chemical Reagent Co., Ltd (Shandong, China). Dimethyl sulfoxide (DMSO) and methanol were obtained from Chuandong Chemical Co., Ltd (Chongqing, China). All the chemicals were used as received. Britton-Robison (BR) buffer was used to control the acidity of the solution in EA detection. Milli-Q purified water (18.2 M Ω cm) was used throughout the experiments.

2.2. Instrumentations

The extinction spectra of AuNRs and Au@Ag core-shell NRs were measured using a UV-2550 UV-vis spectrophotometer (Shimadzu, Japan). Transmission electron microscopy (TEM) images of the nanoparticles and energy dispersive X-ray (EDX) measurement of individual particles were taken using a Tecnai G2 F20 transmission

Download English Version:

<https://daneshyari.com/en/article/7554382>

Download Persian Version:

<https://daneshyari.com/article/7554382>

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