

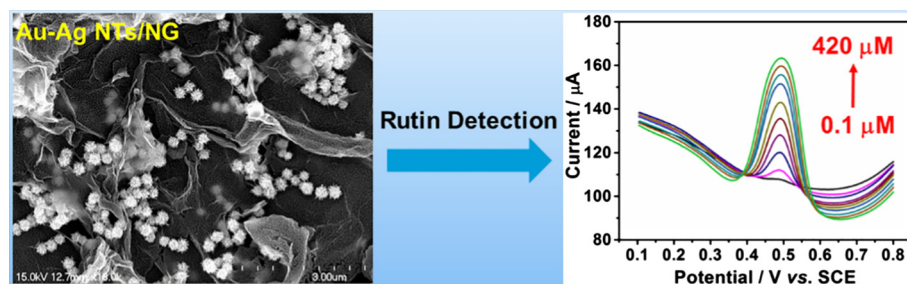
## Regular Article

## A seed-mediated method to design N-doped graphene supported gold-silver nanothorns sensor for rutin detection

Beibei Yang<sup>a,1</sup>, Duan Bin<sup>a,1</sup>, Ke Zhang<sup>a</sup>, Yukou Du<sup>a,\*</sup>, Tetsuro Majima<sup>b,\*</sup><sup>a</sup> College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China<sup>b</sup> The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

## GRAPHICAL ABSTRACT

A novel Au-Ag nanothorns (NT) composite has been synthesized through a seed-mediated mild chemical route, which was found have a linear response in the range of 0.1–420  $\mu\text{M}$  and a comparable detection limit of 0.015  $\mu\text{M}$  ( $S/N = 3$ ) towards rutin detection.



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## ABSTRACT

In this paper, a novel Au-Ag nanothorns (NT) composite has been synthesized through a seed-mediated mild chemical route, and then assembled on N-doped graphene (NG). The composite (Au-Ag NTs/NG) was characterized by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Furthermore, electrochemical activity of as-prepared Au-Ag NTs/NG was investigated by cyclic voltammetry (CV) and different pulse voltammetry (DPV). In CVs of Au-Ag NTs, NG, and Au-Ag NTs electrodes recorded in 0.1 M PBS (pH = 3.0) containing 0.1 mM rutin, a remarkably large peak current (55  $\mu\text{A}$ ) was obtained on Au-Ag NTs/NG compared to those for NG (25  $\mu\text{A}$ ) and Au-Ag NTs (6.2  $\mu\text{A}$ ) demonstrating the remarkably enhanced electrochemical activity of the Au-Ag NTs/NG as compared to Au-Ag NTs/NG and NG modified onto a glassy carbon electrode. Electrochemical measurements indicated that the sensors made by Au-Ag NTs/NG electrode are very sensitive and selective for rutin detection due to the NT structure and effects of NG and Au-Ag NTs. In the DPV, Au-Ag NTs/NG electrode was found to have a linear response in the range of 0.1–420  $\mu\text{M}$  and a comparable low detection limit of 0.015  $\mu\text{M}$  ( $S/N = 3$ ). These results demonstrate that Au-Ag NTs/NG has great potential in extending application in sensor field as the efficient material.

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\* Corresponding authors.

E-mail addresses: [duyk@suda.edu.cn](mailto:duyk@suda.edu.cn) (Y. Du), [majima@sanken.osaka-u.ac.jp](mailto:majima@sanken.osaka-u.ac.jp) (T. Majima).<sup>1</sup> B. Yang and D. Bin are equally contributed to this work.

## 1. Introduction

Rutin (vitamin P) is commonly considered as a kind of bioactive flavonoid glycoside to present broad range physiologic activities

including anti-inflammatory, anti-bacterial, anti-tumor, anti-viral, and anti-oxidant [1,2]. Since rutin has received considerable interest due to its medicinal application in clinical chemistry and human health. In recent years, many analytical methods have been developed for rutin detection, such as electrophoresis, high performance liquid chromatography, capillary electrophoresis spectrophotometric, and even some solid extraction methods [3–5]. However, those methods require relatively complex devices, time-consuming procedure, or poor sensitivity, to hamper their further application.

To prevent deteriorating during accurate rutin detection, a simple, fast, sensitive, and low-cost method is of great significance. Until now, due to the presence of flavonoid glycoside group in rutin structure and its dramatic electroactivity, it is easy for rutin to generate preferable electrochemical response. Electrochemical techniques have offered a better pathway for rutin detection with the advantages of simplicity, sensitivity, wide dynamic range, and possibility to construct portable devices for on-site determination [6]. For example, Sun et al. have provided the excellent electrochemical activity of rutin at graphene (GR)-polymer acridine orange (PAO) modified/carbon ionic liquid paste electrode (CLPIE) than GR/CLPIR and PAO/CLPIR [7]. Liu et al. have fabricated novel SH- $\beta$ -cyclodextrin functionalized graphene-palladium nanoparticles for rutin detection [8]. In current developments, various kinds of nanomaterials including carbon nanotubes, graphene, metal nanoparticles, and metal oxide, have been extensively investigated as electrode modifying agents for electrochemical detection of flavonoids. Especially, two dimensional (2D) nature of graphene has a lot of unique properties such as the largest surface area ( $2630 \text{ m}^2 \text{ g}^{-1}$ ), high conductivity ( $103\text{--}104 \text{ S m}^{-1}$ ), and tunable electron density [9,10]. For instance, in virtue of these advantages, Dong et al. have demonstrated that graphene is attractive sensing material to detect enzymeless glucose [11]. Du et al. have designed a novel graphene based on carbon fiber electrode (CFE) for the sensitive and selective detection of ascorbic acid, dopamine, and uric acid, demonstrating that graphene is an exceptionally low noise and sensitive material towards chemical detection [12].

Zero band gap and absence of dangling bonds of graphene limit the device-based applications. Recently, some pioneering research has been reported on doping of graphene substituted by foreign atoms such as N, P, and B, which affect  $sp^2$  carbon atoms. When C is substituted by N with lone pair electrons, NG has higher free charge-carrier densities and enhanced electrical conductivities [13,14]. Increasing N content in graphene provides more abundant binding sites for non-covalent functionalization to enhance the sensitivity and biocompatibility in biosensing applications [15]. However, for single element doped-graphene, it is difficult to achieve an ideal electrocatalytic performance. Most recently, an electrochemical DNA biosensors based on NG/Au nanoparticles have been successfully employed for human multidrug resistance gene detection [16]. Graphene/metal nanomaterials with catalytic characters of both graphene and metal have received extreme attention from the field of electrochemical sensor. On the other hand, the size, shape, composition, crystallinity, and structure determine the intrinsic properties of metal nanomaterials [17]. Currently, metal nanoparticles (NPs) with interior cavities, controlled shell architectures, hollow structure, or other highly desirable nanostructures, have been broadly used for catalyst and sensor because of their larger surface area and lower density [18,19]. For instance, Shang et al. have prepared hollow PdAu NPs assembled on N-doped graphene (NG) to show superior electrocatalytic activity towards reduction of  $\text{H}_2\text{O}_2$  [20]. Au-Ag bimetallic nanoparticles with different morphologies such as nanorods, nanodendrites, and nanoplates, have been explored for surface-enhanced Raman scattering (SERS) and catalytic activity [21–23]. However, there are only a few reports about the compos-

ite of Au-Ag nanostructure and N-doped graphene. In the present work, Au-Ag nanothorns (Au-Ag NTs) are successfully prepared by L-dopa directly reducing  $\text{HAuCl}_4$  in the presence of spherical Ag nanoparticles as the seeds, thus further assembling on NG. From the electrochemical measurements, Au-Ag NTs/NG modified electrode exhibits an enhanced electrocatalytic activity for rutin detection as compared to Au-Ag NTs and NG.

## 2. Experimental section

### 2.1. Materials

$\text{AgNO}_3$ ,  $\text{HAuCl}_4$ , trisodium citrate dehydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), L-dopa, NaCl,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ ,  $(\text{NH}_4)_3\text{PO}_4$ , KCl,  $\text{Na}_2\text{SO}_4$ , dopamine (DA), ascorbic acid (AA), uric acid (UA), glucose,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$ , and rutin were purchased from Sinopharm Chemicals Reagent Co., Ltd, China. N-doped graphene was purchased from Xianfeng Reagent Co. Ltd. (Nanjing, China). Other reagents were of analytical grade and used as received. Distilled (DI) water was used throughout the whole experiments.

### 2.2. Instrumentation

The scanning electron microscope (SEM) measurements were performed using a Hitachi S-4700 system, and energy dispersive X-ray spectroscopy (EDX) was obtained using a SU1510 SEM (Hitachi Co., Japan). The morphology and structure of the obtained samples were analyzed by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements on a Tecnai G220 electron microscope operating at an accelerating voltage of 200 kV. X-ray diffraction data (XRD) were recorded with a PANalytical X'Pert PRO MRD X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) operated at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALab 220i-XL electronic spectrometer from VG Scientific using 300 W Al  $\text{K}\alpha$  radiation. All voltammetric measurements including cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were executed on an electrochemical workstation (CHI 760E, Shanghai Chenhua, China). A conventional three-electrode system was used with a glassy carbon electrode (GCE, diameter: 3.0 mm, Shanghai Chenhua, China) equipped with 10  $\mu\text{L}$  of the as-prepared catalysts ink. A platinum wire and saturated calomel electrode (SCE) were served as the counter electrode and the reference electrode, respectively.

### 2.3. The growth of Ag seeds

The silver seeds were successfully prepared according to the typical method [24]. In a brief, 9.0 mg  $\text{AgNO}_3$  was added into a three-neck round flask with 50 mL DI water and heated with an oil bath at  $100^\circ\text{C}$  under magnetic stirring bar. Once the solution was boiled, 5.0 mg  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  was added into the above mixture. After the mixed solution was boiled for another 2 min, the color of solution changed from colorless to bright yellow immediately. Heating and stirring continued for an additional 20 min, the color of mixture gradually changed to grayish green. Finally, after cooling down to room temperature, Ag seeds were collected and fixed at 50 mL DI water.

### 2.4. Synthesis of Au-Ag nanothorns on N-doped graphene (Au-Ag NTs/NG)

2.5 mg of NG was dispersed in 5.0 mL of ethanol with ultrasonication for 30 min to form a homogenous solution. 1 mL  $\text{HAuCl}_4$  aqueous solution (24 mM) was mixed with 4.0 mL DI water in a

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