



Immobilization and electrocatalysis of Ru(III) ions on phosphonate functionalized gold nanoparticles



Pan Li^a, Zhaoyang Lu^a, Dongmei Sun^a, Chenxin Cai^a, Shaohua Wei^{a,*}, Yu Chen^b, Jong-Min Lee^{b,**}

^a Jiangsu Key Laboratory of New Power Batteries, Jiangsu Collaborative Innovation Centre of Biomedical Functional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China

^b School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore

ARTICLE INFO

Article history:

Received 19 November 2014

Received in revised form 17 January 2015

Accepted 20 January 2015

Available online 21 January 2015

Keywords:

Phosphonate

Chemical functionalization

Gold nanoparticles

Ruthenium

Iodate

ABSTRACT

The surface chemical functionalization generally endows gold nanoparticles (Au-NPs) with expanding applications in sensors, medicine and catalysis because of the synergistic effect. In this work, we report a novel strategy for the synthesis of phosphonate functionalized Au-NPs (P-Au-NPs) by using vinylphosphonic acid as the reducing agent and stabilizing agent. The morphology, composition, and structure of P-Au-NPs are fully characterized by various spectroscopy techniques. The resultant P-Au-NPs show a remarkable colloidal stability, which likely arises from strong electrostatic effect of negatively charged phosphonate groups and the extremely hydrophilic property of phosphonate groups. In addition, the as-prepared P-Au-NPs effectively bind Ru^{III} ions via coordination interaction, which can be used to construct an iodate amperometric sensor with the wide linear range and low detection limit.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Gold nanoparticles (Au-NPs) have received increasing attention in the past decades because of their chemical inertness, biocompatibility, as well as unique optical and catalytic properties [1–4]. Surface chemical functionalization of Au-NPs with tactical molecules not only effectively prevents their aggregation but also largely expands their potential applications in various fields such as optical devices, bioimaging, biological labeling, sensors, and catalysis, owing to the synergistic effect between functional molecules and Au-NPs [5–10].

The phosphonic acid group, $-\text{PO}_3\text{H}_2$, has fascinating chemical properties such as the dibasic nature, excellent hydrophilic property, strong coordination binding capability for metal ions, and particular hydrogen-bonding interaction between $-\text{PO}_3\text{H}_2$ and $-\text{NH}_2$ groups [11–14]. Thus, the phosphonate functionalization endows NPs with high negative charge density over a wide range of pH values, excellent colloidal stability in an aqueous solution, effective metal-ion chelating capability, and good biocompatibility for biomolecules immobilization [15–18]. Such phosphonate functionalized NPs have

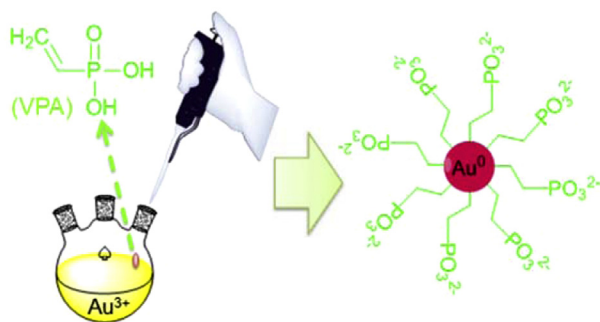
shown highly intriguing applications in catalysis [19,20], sensing [21], bioelectrochemistry [22], electroanalysis [17], etc. Up to now, the phosphonate functionalized Au-NPs (P-Au-NPs) can be easily obtained by using $-\text{PO}_3\text{H}_2$ -terminated thiols molecules as a stabilizer [14]. Although early studies contemplated that thiolates-self-assembly monolayers (SAMs) were extraordinarily inert under ambient conditions, recent reports showed that the Au–S bond could be oxidized to sulfinate and/or sulfonate at ambient conditions due to O_2 in air [23,24]. Thus, the quality and structure of the thiolates-SAMs could be perturbed due to oxidation, and consequently restrained their applications. In addition, the synthesis of the $-\text{PO}_3\text{H}_2$ -terminated thiols is difficult, which also restrains the development of the P-Au-NPs.

Iodine plays an important role in cell growth and brain function. An accurate, rapid, and low-cost determination of iodate is important in the field of food, drugs, and industrial applications [25,26]. The previous reports have demonstrated that both Ru oxide [25] and Ru complex [26] have excellent electrocatalytic activity for the iodate reduction. In this work, we demonstrate that P-Au-NPs can be conveniently synthesized by using vinylphosphonic acid (VPA, Scheme 1) as a reducing agent and a stabilizing agent. The as-prepared P-Au-NPs show strong coordination binding ability for Ru^{III} ions. The immobilized Ru^{III} ions show excellent electrocatalytic activity for the reduction of iodate, hence it can be used to construct an electrochemical sensor for iodate detection.

* Corresponding author. Tel.: +86–25–85891651; fax: +86–25–83243286.

** Corresponding author. Tel.: +65–6513–8129; fax: +65–6794–7553.

E-mail addresses: weishaohua@njnu.edu.cn (S. Wei), jmlee@ntu.edu.sg (J.-M. Lee).



Scheme 1. Schematic illustration of the synthesis of P-Au-NPs.

2. Experimental

2.1. Materials

Vinylphosphonic acid (VPA, [Scheme 1](#)) was provided by Sigma Co. Ltd. Auric acid (HAuCl_4), ruthenium trichloride (RuCl_3) and potassium iodate (KIO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd. Other reagents were of analytical grade and used as received. Solution of pH 2.0 K_2SO_4 - H_2SO_4 was prepared from 0.1 M K_2SO_4 by adjustment with 0.5 M H_2SO_4 . All the aqueous solutions were prepared with Millipore water having a resistivity of 18.2 M Ω .

2.2. Synthesis of phosphonate functionalized gold nanoparticles (P-Au-NPs)

In a typical synthesis, 25 mL of 0.58 mM HAuCl_4 aqueous solution (pH 9.0) was added to three-neck flask equipped with a reflux condenser and heated to 100 °C. Then, 1 mL of 73 mM VPA solution (pH 9.0) rapidly added to the HAuCl_4 solution and mechanically stirred for 10 min until the color of the solution changed to red and no further color change occurred. The as-prepared P-Au-NPs colloidal solution was stored under refrigerated dark conditions before and after use.

2.3. Preparation of Ru^{III} /P-Au-NPs/GC electrode

The glassy carbon electrode (GC, 3 mm in diameter, CH Instruments) was served as the working electrode. Ten microliters of the as-prepared P-Au-NPs colloidal solution was loaded onto the clean GC electrode surface and then dried at room temperature. After deposition, the obtained P-Au-NPs/GC electrode was immersed into Millipore water for 20 min to remove the free VPA and then dried with nitrogen gas. Immobilization of Ru^{III} ion on P-Au-NPs/GC electrode was accomplished by immersing the P-Au-NPs/GC electrode in a RuCl_3 solution (46 mM, pH 0.85) for 24 h at room temperature. After washing and drying, the working electrode denoted as Ru^{III} /P-Au-NPs/GC was obtained.

2.4. Electrochemical measurements

All electrochemical experiments were carried out on a CHI 660C electrochemical workstation (CH Instruments, Shanghai, Chenghua Co.) in a conventional three-electrode electrochemical cell. A Pt plate auxiliary electrode and a saturated calomel reference electrode (SCE) were used. All potentials in this study were reported with respect to SCE. Prior to the electrochemical measurements, N_2 was bubbled through the solution for 10 min to remove the dissolved O_2 . During experiments, a continuous N_2 flow was maintained over the solution. All the electrochemical

measurements were carried out at 25 ± 1 °C in a water-jacketed glass vessel connected to a circulating water bath.

2.5. Physical characterization

Ultraviolet-visible spectroscopy (UV-vis) measurements were recorded at room temperature on a Shimadzu UV3600 spectrophotometer. Transmission electron microscopy (TEM) measurements were made on a JEOL JEM-2100F transmission electron microscopy operated at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were obtained with Model D/max-rC X-ray diffractometer. Fourier transform infrared (FT-IR) spectra were carried out using a Nicolet 520 SXFTIR spectrometer. The zeta potential measurements were performed with a Malvern Zetasizer Nano ZS90 analyzer at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo VG Scientific ESCALAB 250 spectrometer. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV.

3. Results and discussion

3.1. Synthesis of P-Au-NPs

In a typical synthesis, P-Au-NPs were obtained by injecting VPA solution into a boiling HAuCl_4 solution (feeding molar ratio of VPA/ HAuCl_4 is 5:1) under vigorous stirring conditions ([Scheme 1](#)). During the process, the colour of the reaction solution was gradually changed from light yellow to deep pink within 12 min, which is indicative of the formation of Au-NPs (insert in [Fig. 1](#)). The growth process of the Au-NPs was monitored by time-dependent UV-visible spectrum (UV-vis) measurements ([Fig. 1](#)). During the reaction, the localized surface plasmon resonance (SPR) of Au-NPs gradually grew with time. After approximately 10 min, the SPR absorbance value reached a maximum and peak position ($\lambda = 519.5$ nm) remained constant, indicating the HAuCl_4 had been reduced completely. Similar to oleylamine-mediated synthesis of Au-NPs [27–29], the C=C double bond in VPA may be responsible for the reduction of HAuCl_4 due to its weak reducibility.

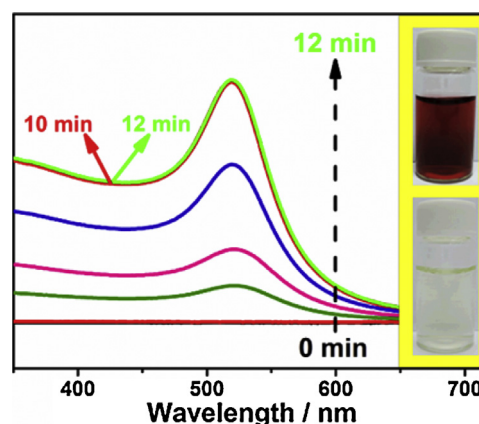


Fig. 1. UV-vis spectra of HAuCl_4 solution (pH=9.0) at different stages after the injection of VPA (pH=9.0). Measurement conditions: UV-vis measurements were performed by adding 3 mL of 3-fold diluted reaction solution at different stages into in a quartz cuvette having 1 cm path length at room temperature. Light yellow bottle: HAuCl_4 solution; Red bottle: the as-prepared P-Au-NP colloidal solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/184631>

Download Persian Version:

<https://daneshyari.com/article/184631>

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