Journal of Electroanalytical Chemistry 631 (2009) 58–61

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Comparison of spherical nanogold particles and nanogold plates for the oxidation of dopamine and ascorbic acid

Rajendra N. Goyal [a,*], Akrajas Aliumar [b], Munetaka Oyama [c]

[a] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India
[b] Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[c] Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan

ARTICLE INFO

Article history:
Received 22 December 2008
Received in revised form 24 March 2009
Accepted 24 March 2009
Available online 1 April 2009

Keywords:
Nanogold
Voltammetric determination
Dopamine
Ascorbic acid

ABSTRACT

Spherical gold nanoparticles of different size and Au nanoplates were grown at indium tin oxide surface and characterized using SEM. The application of different electrodes in voltammetry for determination of dopamine and ascorbic acid indicated that oxidation of these biomolecules occur at these electrodes in diffusion controlled process and Au nanoplates modified indium tin oxide electrodes exhibit atleast two to three times higher current than spherical nanogold particles of different size. The observed behaviour suggests that Au nanoplates exhibit higher electrocatalytic activity than spherical gold nanoparticles. The reason for such a behaviour may be due to their (1 1 1) lattice plane as the basal plane as well as due to more available surface edges. As dimensions of nanoplates is of the order of 400–500 nm, the increased surface area in the case of nanoplates also appears to play a significant role.

1. Introduction

The nanomaterials modified electrodes have attracted considerable attention in last few years as sensors and biosensors for variety of biomolecules and metal ions [1–3]. Nanogold or single or multi-walled carbon nanotube modified electrodes are two common electrodes widely used for these purposes [4–7]. Recently, the nanomaterial-composite modified electrodes have been claimed to exhibit much higher sensitivity in comparison to only nanomaterials modified electrodes [8,9]. This laboratory is preparing nano-Au and -Ag particles of different shape and size from last few years in the expectation that electrodes fabricated using these nanoparticles would exhibit catalytic properties towards oxidation of biomolecules. The usefulness of these nanoparticles is further enhanced if they are deposited on substrate like indium tin oxide (ITO). Such electrodes have been proved as an excellent working electrode having properties such as high electroactive surface area, excellent electronic conductivity and wide available potential window. The applications and catalytic properties of nanogold modified indium tin oxide electrode have already been demonstrated in recent years in the determination of dopamine, uric acid and many other biologically important compounds [7,10].

In this communication an attempt has been made to prepare spherical nanogold particles of different sizes and compare the electrochemical behaviour of two biologically important compounds viz., dopamine and ascorbic acid at spherical nanogold modified ITO electrodes with Au nanoplate modified electrode. Three different sizes of spherical nanogold particles (20 nm; medium 20–50 nm and large 50–100 nm) were prepared. It is observed that the peak currents observed at Au nanoplate modified ITO electrode are nearly two to three times larger than observed for spherical gold nanoparticles modified ITO electrode. It is thus expected that the sensitivity and detection limit will be much better at Au nanoplate modified ITO electrode in linear sweep voltammetry, differential pulse voltammetry and Osteryoung square wave voltammetry in comparison to spherical nanogold particles.

2. Experimental

Dopamine, ascorbic acid, cetyltrimethylammonium bromide and $HAuCl_4$ were obtained from Sigma–Aldrich, USA. ITO coated glass plates were procured from CBC Optics. Ltd., Japan, and used by cutting into pieces of ca. 10 mm × 10 mm. FE-SEM images were recorded using a field emission scanning electron microscopy model JSF 7400F JEOL.

The detailed procedure to attach and growth of Au nanoparticles or nanoplates on the surface of ITO has been described earlier [11,12]. For Au nanoparticles, in brief, a piece of ITO was immersed first in a seed solution containing ca. 4 nm Au nanoseed particles, and then in a growth solution containing cetyltrimethylammonium bromide (CTAB), $HAuCl_4$, ascorbic acid and NaOH solution. In the present work, the grown sizes of Au nanoparticles were controlled by changing the time in the growth solution. In this seed

* Corresponding author. Tel.: +91 1332 285794; fax: +91 1332 273560.
E-mail address: rngcyfcy@iitr.ernet.in (R.N. Goyal).

0022-0728/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2009.03.013

mediated growth procedure, when another growth solution containing $HAuCl_4$ and poly(vinylpyrrolidone) (PVP) was used, we could prepare Au nanoplate-attached ITO substrates as reported previously [12]. In the present work, to increase the coverage amount of Au nanoplates, the contents of the growth solution used was prepared by adding 0.1 ml of 0.1 M ascorbic acid into a solution that contained 0.5 ml of 0.01 M $HAuCl_4$, 10 ml of 1 mM PVP, 8 ml of 0.1 M CTAB and 2 ml pure water, and then a piece of ITO was immersed for 18 h after the seeding treatment. As wet chemical method was used for preparation of Au nanoplates, a few nanorods and spherical nanoparticles were also formed.

To evaluate the electrochemical properties of the Au nanoparticle or nanoplate-attached ITO, it was used as working electrode. For this purpose, the modified ITO was connected to a strip of copper adhesive tape and then molded in a piece of scotch tape for mending which was made to have a 2 mm diameter hole. For the electrochemical measurement, the exposed area of $\sim\bar{2}.0$ mm dia contacted the solution.

The electrochemical experiments were performed using an EG&G M263A potentiostat/galvanostat (Princeton Applied Research) controlled by a computer with M270 program. An Ag/AgCl reference electrode (BAS) and a platinum wire auxiliary electrode were used.

Stock solutions of dopamine and ascorbic acid (1 mM) were prepared in phosphate buffer of pH 7.2 (μ = 0.5 M) and voltammograms were recorded after bubbling nitrogen for 10 min. Many times it was noticed that due to air bubble at the surface of hole, the contact between electrode and solution becomes weak, in such cases the electrode was tapped to remove air bubble or nitrogen was bubbled at the side of hole to remove air bubble. The electrode was cleaned before each run in each case by applying a potential of -100 mV for 30 s to desorb any material adsorbed at the surface of electrode.

3. Results and discussion

It was observed [11,12] during preparation of nanogold particles that seed mediated growth approach leads to growth of spherical nanoparticles of different size (20–100 nm) depending upon the time allowed in the growth solution. In the present studies the time allowed in growth solution was 30 min, 1 h and 24 h. At these times spherical nanogold particles of different size were deposited. They have been named as small (<20 nm), medium (20–50 nm) and large (>50 nm) nanogold particles. On the other hand by changing the growth solution to $HAuCl_4$ and poly(vinylpyrrolidone) the 2D growth of nanocrystals proceeded. In such a case single crystalline Au nanoplates with (1 1 1) basal plane and the edge length up to ca. 2 μm, growing parallel to the surface of ITO are observed as reported earlier [12]. The FE-SEM images of different spherical nanoparticles and nanoplates grown on indium tin oxide are presented in Fig. 1A–D and clearly indicate the deposition of spherical and nanogold plates. Initially the response of different electrodes prepared was monitored for ferrocyanide by recording linear sweep voltammograms. Fig. 2 presents a comparison of voltammograms at gold nanoparticles attached electrode with bare gold electrode at sweep rate of 20 mV s^{-1}. The current magnitude of ferrocyanide at ITO electrode is presented by curve a in Fig. 2, whereas, at bare gold electrode is presented by curve c. The curves b and d present current magnitude of spherical Au nanoparticles (>50 nm) and nanoplates. It is clear from the figure that for the standard redox couple the response of nanoplates is larger in comparison to spherical Au nanoparticles and the current would not depend on the 2D surface of the gold. To compare the electrochemical behaviour of two common biomolecules, the differential pulse voltammograms of dopamine and ascorbic acid were recorded at these electrodes. Fig. 3 presents a comparison of voltammograms observed for ascorbic acid at pH 7.2. It was observed that electrodes having spherical nanogold particles of

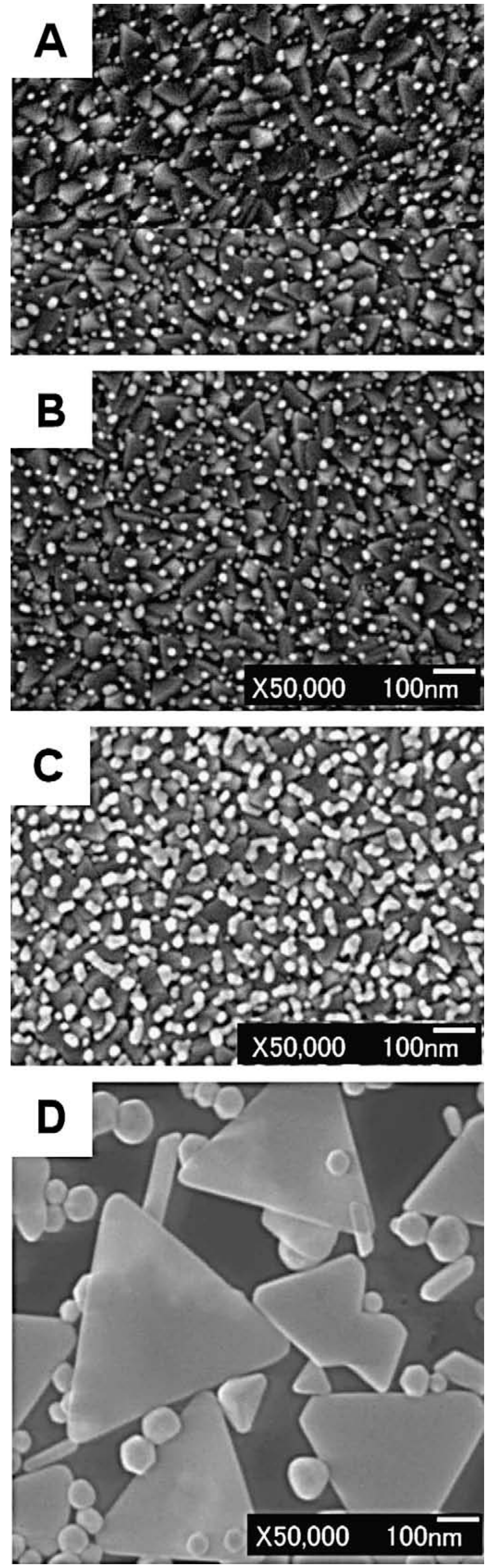

Fig. 1. Typical FE-SEM images of nanogold modified ITO electrodes (A) after 30 min, (B) after 1 h, (C) after 24 h of crystal growth and (D) after changing growth solution to $HAuCl_4$ and poly(vinylpyrrolidone).