Advanced Materials Research
ISSN: 1662-8985, Vols. 926-930, pp 190-193
doi:10.4028/www.scientific.net/AMR.926-930.190
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Online: 2014-05-23

Progress in fabrication and application of gold nanoparticles modified indium tin oxide glass

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Keywords: Gold nanoparticles, ITO substrate, preparation, application.

Abstract. Gold nanoparticles coated on indium tin oxide substrate have been attracting great attention due to their excellent optical, electronic, electrocatalytic and biosensing application in recent years. In this paper, recent research progress in the preparation methods of gold nanoparticles on indium tin oxide substrate surface such as assembling with polymer, seed-mediated growth method and electrodeposition are presented. The applications of gold nanoparticles modified indium tin oxide substrate are also reviewed in electrode, catalyst, sensors and biochemical analysis.

Introduction

In recent years, metal nanoparticles coated on solid substrates have been attracting increasing attention on account of their unique optical, electronic, catalytic properties and biosensing application [1-4]. Among various metal nanoparticles, gold nanoparticles (GNPs) have received extensive studies for their good conductivity, high surface area, excellent biocompatibility and useful catalytic activity, which lead to the rapid expansion of gold nanoparticles modified electrodes or biosensors [5-10]. It is necessary to immobilize the nanoparticles on a substrate for better stability of gold nanoparticles and that provides consistent and stable sensor response. A variety of suitable solid substrates are reported in the literatures to fabrication gold nanoparticles modified electrodes or sensors, such as silica, glassy carbon and indium tin oxide (ITO). Among these solid substrates, ITO substrate is of great interest because of its prominent characteristics such as good electrical conductivity, high optical transparency, wide electrochemical working window, excellent substrate adhesion, and stable electrochemical and physical properties [11-13]. ITO substrate could also be available at a very low cost from industrial mass production, which is very important in sensor design and manufacture. In this article, the research progress in preparation and application of gold nanoparticles modified ITO glass is described.

Fabrication methods of GNPs modified ITO glass

Assembling with polymer. Gold nanoparticles can be synthesized on the surface of the ITO substrate by a variety of different strategies. Assembling with polymer is based on specific binder molecules, such as (3-mercaptopropyl) trimethoxysilane (MPTMS) and (3-aminopropyl) trimethoxysilane (APTMS), which utilizes the binding ability of the silanol group to the surface of ITO substrate and affinity of the –SH or $–NH_2$ group towards the GNPs. MPTMS modified ITO glass has been employed by Cheng et al. for the synthesis of gold nanoparticles [14]. Wang et al. synthesized 15nm colloidal gold particles on the surface of ITO substrate, which was modified with APTMS to yield an interface for the assembly of colloidal gold [15]. It is found that the characteristics of GNPs obtained by this way, such as conductivity and catalytic ability, were strongly affected by the organic binder molecules. Fig.1 illustrates the preparation procedure of GNPs modified ITO substrate by assembling with APTMS.

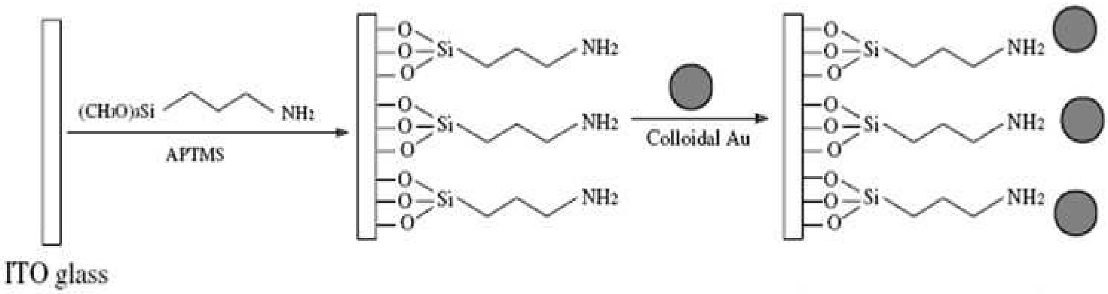

Fig.1 Preparation procedure of GNPs modified ITO substrate by assembling with APTMS. Reprinted with permission from ref 15 (Wang's group). Copyright 2004 Electrochemistry Communications.

Seed-mediated growth method. To overcome the disadvantage of assembling with polymer, Oyama et al. developed seed-mediated growth method to attach gold nanoparticles onto ITO substrate without using organic linker [16-18]. The seed-mediated growth method is divided into "touch" seed-mediated growth and "cast" seed-mediated growth. There are two basic steps for this method: the attachment of nano-seed particles onto the ITO surface by immersing the ITO electrode into the stock solution containing small colloidal gold particles about 4nm and the growth of them in growth solution include cetyltetrammonium bromide (CTAB), $HAuCl_4$ and ascorbic acid. This method is somewhat complex and time-consuming, thereby limiting their applicability to the mass production. Fig.2 shows the preparation procedure of GNPs modified ITO substrate by cast seed-mediated growth method.

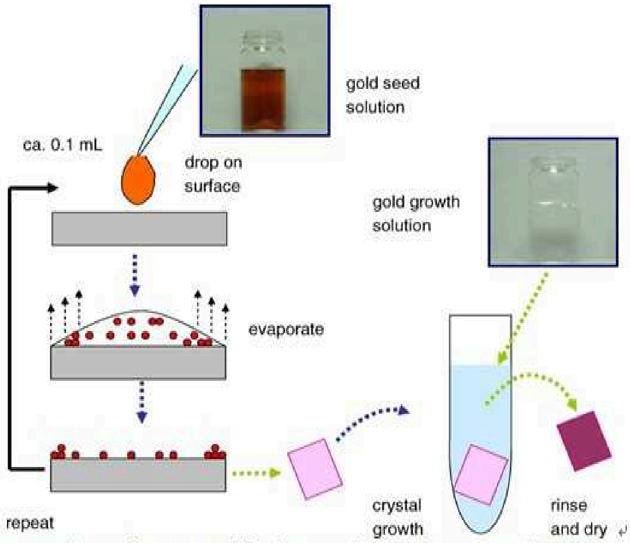

Fig.2 Preparation procedure of GNPs modified ITO substrate by cast seed-mediated growth method. Reprinted with permission from ref 18 (Oyama's group). Copyright 2006 Applied Surface Science.

Electrodeposition. Electrodeposition is a very powerful technique for the synthesis of GNPs on the ITO substrate due to rapid and simple. Electrodeposition method includes constant current, constant voltage, cyclic voltammogram, and so on. By varying the deposition potential or current, deposition time, concentration, and buffer solution one can control the size, shape and distribution of GNPs. In 2006, GNPs modified ITO film coated glass electrode has been fabricated for the first time via direct electrodeposition from 0.5 M H_2SO_4 containing 0.1 mM $AuCl_4^-$ in the work of Dai et al [19]. In this article, since the electrodeposition is too rapid to provide rigorous control of the growth of nanoparticle size, the electrodeposition of nanoparticle size may range from tens of nanometers to hundreds of nanometers. Di and co-works used cyclic voltammogram method to electrodeposit GNPs on the surface of ITO substrate from an electrolytic bath that comparised $HAuCl_4$ and the phosphate buffer solution [20-22]. The authors found that the shape of GNPs would be modified to form twin-linked or more-connected structures by addition of one of deposition cycles, concentration, and deposition temperature, or decreasing the deposition potential during the electrolysis. The twin-linked or more-connected gold nanoparticles were found to have excellent electrochemical properties in addition to be a sensor for the detection of specific target biomolecules.

Application of GNPs modified ITO glass

Application of gold nanoparticles modified ITO galss (GNPs/ITO) include electrocatalysis, determination of metal ions, sensor and biochemical analysis. Jaramillo et al. have reported the size-dependent electro-oxidation of carbon monoxide (CO) as the first example of catalytic activity from gold nanoparticles synthesized by assembling with polymer in 2003[23]. Oyama and co-works described an improved seed-mediated growth approach for the direct attachment and growth of mono-dispersed GNPs on ITO surfaces and demonstrated that a linear relationship existed between the catalytic current and the concentrate of nitrite, which exhibited a low detection limit for NO sensing on the GNPs [17]. GNPs modified ITO glass was used for the reduction of H_2O_2 by several research groups. For example, Zhang developed a mediator-free H_2O_2 sensor based on the catalytic activity of myoglobin immobilized on a GNPs modified ITO electrode toward the reduction of H_2O_2, a linear relationship was found between the catalytic current and the H_2O_2 concentration in the range of 2.5×10^{-6}—5×10^{-4} M with a detection limit of 4.8×10^{-7} M [24]. Dai et al. employed GNPs modified ITO electrode prepared by direct electrochemical deposition to detect arsenic (Ⅲ) through linear sweep voltammetry for the first time [19]. The GNPs modified ITO glasses were applied to development of refractive index (RI) sensors for variety of organic solvents in the work of Wang, it is demonstrated that the RI sensors is of higher sensitivity based on the larger GNPs [21]. GNPs/ITO as a base for the immobilization of enzymes or antigens has been widely used to prepare biosensor with horseradish peroxidase, cytochrome c, glucose oxidase, superoxide dismutase (SOD) and so on. As an example, Deng et al. reported a bioconjugation of GNPs/ITO with goat anti-mouse-immunoglobulin G （anti-m-IgG） is successfully employed for the detection of mouse-immunoglobulin G (m-IgG) in a mode based on the specific binding affinity between the antigen and antibody. This study reveals a simple and sensitive method to fabricate a label-free optical biosensor based on the localized surface plasmon resonance of GNPs on ITO substrate [22].

Conclusions

An overview of the fabrication and application of gold nanoparticles modified ITO glass (GNPs/ITO) are presented in this article. GNPs modified ITO glass is widely applied in the field of catalyst, sensors and biochemical analysis due to its prominent characteristics and low cost, especially, connected GNPs revealed excellent performance in biosensor. Electrodeposition method is more simple and rapid in comparison with assembling with polymer and seed-mediated growth method, and avoided the effect of organic molecules on conductivity and catalytic ability. However, there are few reports on the detailed mechanism of the direct electrodeposition of GNPs onto ITO surface. The understanding of the mechanism is conducive to optimizing the performance of GNPs. Therefore, future research will need to determine the detailed mechanism of deposition of GNPs. Overall, GNPs modified ITO glass will play an increasing important role in the field of electrochemical and biochemical.

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