



Short communication

Fast growth of gold nanorods on solid substrate using electrochemically deposited gold seeds



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ABSTRACT

Growth of gold nanorods (GNRs) on indium–tin–oxide (ITO) substrate was achieved within 4 h using in-situ electrochemical reduction of Au^+ ions from the growth solution. The electrochemically deposited gold nanoparticles on ITO substrate act as the seeds for the growth of GNRs. The yield of GNRs on ITO substrate increases with increasing the concentration of Ag^+ ions in growth solution. Further, the GNRs grown on ITO substrate showed shape dependent surface enhanced Raman scattering enhancement towards 4-aminothiophenol adsorbed on GNR surface.

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1. Introduction

In recent years, much attention has been directed towards the synthesis of anisotropic gold nanostructures such as nanorods, nanoprism, and nanopods due to their tunable optical and electronic properties [1]. Electrochemical, photoirradiation, ultrasonic irradiation and seed-mediated growth processes have been widely employed for the synthesis of gold nanostructures in solution [2]. Compared to other anisotropic nanostructures, gold nanorods (GNRs) received considerable attention due to their novel physical and chemical properties [3]. The tunable optical property of GNRs finds potential applications in signal amplification in bioanalysis and surface enhanced Raman scattering (SERS) [4]. For the catalytic and signal amplification applications, the synthesized anisotropic nanostructures must be immobilized on solid surfaces [5]. Although the growth of GNRs was well-established in solution, only little effort has been taken by the researchers for the growth of GNRs on solid substrates [6–12]. The strategies used for the growth of GNRs on solid substrate include either potential controlled electrodeposition of GNRs from a solution containing cetyltrimethylammonium bromide (CTAB) and HAuCl_4 [13] or attachment of seed particles on thiol or amine functionalized binder molecules on solid substrate followed by immersion of substrates in the growth solution [6–12]. Although these strategies have been successfully used for the growth of GNRs on solid substrates, the yield of GNRs is low due to the formation of other anisotropic nanostructures [6–12]. Here, the yield refers to the ratio between

the number of GNRs to the total number of gold nanostructures. Moreover, it is expected that the binder molecules significantly affect the nature and conducting properties of modified substrates. To overcome these drawbacks, we have developed a novel method for growing GNRs on indium–tin–oxide (ITO) substrate without any linker by in-situ electrochemical reduction of Au^+ ions from the growth solution.

Electrochemical route to the solution based synthesis of GNRs was first reported by Wang and co-workers whereas Zamborini and Abdelmoti first reported the potential controlled growth of GNRs on ITO substrate as a function of electrode potential and deposition time [12,13]. Although the high yield of GNRs was observed in solution, the yield of GNRs grown on ITO substrate is low in the potential controlled growth of GNRs. Thus, the objective of the present study is to grow GNRs on ITO substrates with high yield. Previously, El-Sayed and co-workers reported the in-situ generation of gold seeds in the growth solution for the synthesis of GNRs in solution by adding NaBH_4 [13]. In this case, NaBH_4 reduced Au^+ ions into Au^0 in the growth solution and then further nucleation and growth took place at the generated seed particles resulting in the formation of GNRs [13]. In the present study, we have taken ITO substrate as the working electrode and the GNR growth solution as the electrolytic solution. The seed particles have been electrochemically deposited on ITO substrate by the in-situ reduction of AuCl_2^- -CTAB complex from the growth solution. The deposited AuNPs on ITO substrate act as the nucleation center for the growth of GNRs on ITO substrate. The growth of GNRs was observed within 4 h on ITO substrates. Further, the SERS property of as prepared GNRs on ITO substrate was evaluated using the probe molecule, 4-aminothiophenol (ATP).

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2. Experimental section

2.1. Materials

Hexadecyltrimethylammonium bromide (CTAB), silver nitrate (AgNO_3), hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), ascorbic acid (AA) and 4-aminothiophenol (ATP) were purchased from Sigma-Aldrich and were used as received. Indium–tin oxide (ITO) plates were purchased from Asahi Beer Optical Ltd., Japan.

2.2. Instrumentation

The electrochemical measurements were performed in a conventional two-compartment three-electrode cell with ITO substrate as a working electrode, platinum wire as a counter electrode and NaCl-saturated Ag/AgCl as a reference electrode. Raman spectra were recorded on a Bruker Senterra dispersive Raman microscope with laser excitation wavelength of 516 nm. Surface enhanced Raman spectra were recorded on a Horiba JY LabRAM HR800 Raman spectrometer coupled with microscope in reflectance mode with 633 nm excitation laser sources and a spectral resolution of 0.3 cm^{-1} . The tapping mode AFM images were recorded using a multimode scanning probe microscope (NTMDT, NTEGRA prima, Russia). The electrochemical measurements were carried out with a CHI electrochemical workstation (Model 643B, Austin, TX).

2.3. Electrochemical deposition of gold seeds

The growth solution was prepared according to the reported procedure [14]. For the electrochemical generation of seed particles, the potential was stepped from $+0.6$ to -0.8 V using differential pulse voltammetry (DPV) or linear sweep voltammetry at a scan rate of 20 V s^{-1} by taking ITO as the working electrode, Pt wire as the counter electrode, Ag/AgCl (NaCl sat) as the reference electrode and the

growth solution of GNRs as the electrolytic solution where CTAB acts as the electrolyte at 25°C . After the electrochemical deposition of seed particles, the set-up was left undisturbed for 4 h (Fig. 1A).

3. Results and discussion

3.1. Characterization of GNRs grown on ITO substrates by UV–visible spectroscopy

Fig. 1B shows the differential pulse voltammogram obtained for the reduction of Au^+ ions from the growth solution containing $80 \mu\text{M}$ AgNO_3 using ITO electrode. A cathodic peak was observed at -0.60 V due to the reduction of AuCl_2^- -CTAB complex. This set-up was left undisturbed for 4 h. During this period, the color of the ITO substrate slowly turned into a violet color indicating the growth of gold nanostructures. After 4 h, the ITO substrate was rinsed with water and then UV–visible spectrum was recorded. It shows two well defined absorption bands at 532 nm and 690 nm, due to the transverse and longitudinal plasmonic bands of GNRs, respectively (Fig. 1C). The AuCl_2^- -CTAB complex was electrochemically deposited as metallic gold on ITO substrate which acts as the seeds for the growth of GNRs directly on the surface of ITO substrate. Similar to solution based seed mediated synthesis of GNRs, the electrodeposited seed particles catalyze the reduction of Au^+ ions to Au^0 through which the growth process takes place on ITO substrate. After 4 h, the colorless growth solution slowly changed into reddish pink due to the formation of GNRs in solution and hence further growth of GNRs on ITO surface was not observed. In order to find the role of electrochemically deposited seeds for the growth of GNRs, the bare ITO substrate was immersed into the growth solution under similar conditions. The colors of both the ITO substrate and the growth solution were not changed indicating that the GNRs were not grown on both ITO substrate and in solution. This concluded that the electrochemically generated seeds induced the growth of GNRs both in solution and substrate.

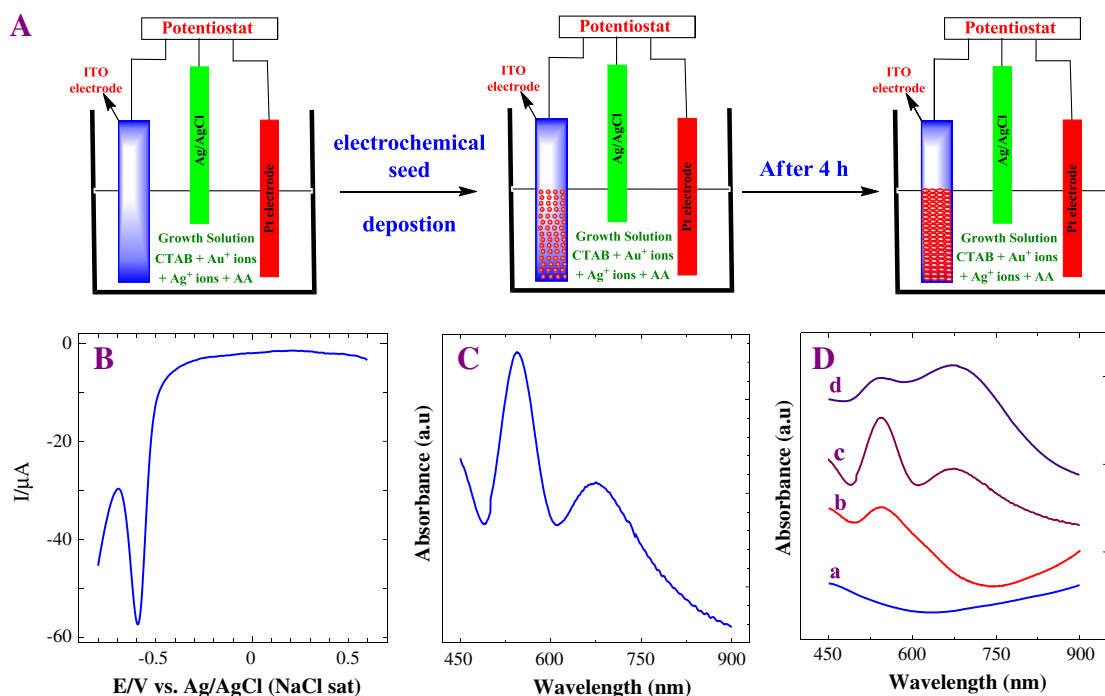


Fig. 1. (A) Schematic illustration for the growth of GNRs on ITO substrate, (B) electrochemical in-situ reduction of Au^+ ions from the growth solution on ITO substrate, (C) UV–vis spectrum of electrochemically generated seed deposited ITO substrate after 4 h of immersion in growth solution and (D) UV–vis absorption spectra obtained for (a) seed deposited ITO electrode and GNRs grown on ITO electrode after 4 h of immersion in growth solution from electrochemical deposition of seed particles from the growth solution containing (a) 0, (b) $80 \mu\text{M}$ and (c) $160 \mu\text{M}$ AgNO_3 .

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