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Large-area plasmonic electrodes and active plasmonic devices generated by electrochemical processes

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ABSTRACT

This work describes a fast electrodeposition method for generating gold plasmonic electrodes and their use as active plasmonic devices. Gold nanoparticles (AuNPs) are easily obtained on large areas (up to several square centimeters) on indium tin oxide (ITO) electrodes using electroreduction of an Au^{III} salt by chronoamperometry. These AuNP substrates exhibit a strong localized surface plasmon resonance (LSPR) signal in the visible range, and constitute low-cost plasmonic electrodes. The average size, the density and the dispersity of the AuNPs, as seen by scanning electron microscopy (SEM), can be modulated by the potential applied during electroreduction. In this way, the LSPR can be varied from 680 nm to 580 nm with a concomitant marked evolution of the full-width at half-maximum from 200 to 80 nm. An important result is that the LSPR of substrates generated at -0.9 V using a charge density of 20 mC cm^{-2} is close to that of AuNP gratings obtained using e-beam lithography. In a second step, the best AuNP-modified electrodes were covered with an ultrathin organic film of bithienylbenzene (BTB) generated by electroreduction of the corresponding diazonium salt. This film switches between a conducting and an insulating state depending on the applied voltage. The effect of the switch on the plasmonic properties of AuNPs is reported. Despite the small thickness of the film (below 15 nm), its conductance switch leads to a reversible modulation of the LSPR intensity by as much as 25%.

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1. Introduction

Research on nanoscale materials has intensified during the past decades, due to the increasing demand for ultimate miniaturization of electronic and photonic systems. Noble metal (gold and silver) nanoparticles (NPs) have been particularly well investigated, because of their remarkable optical properties. Indeed, particles smaller than the incident light wavelength exhibit collective oscillations of their free electrons, leading at a particular frequency to a resonance phenomenon, known as localized surface plasmon resonance (LSPR). This results in a strong optical extinction in the visible or the near-infrared spectral regions. The optical behavior, defined by the resonance wavelength, the bandwidth and the amplitude of the LSPR, depends on the size of the NPs, their shape, and the dielectric constant of the surrounding medium. Active plasmonic devices, *i.e.* plasmonic systems for which an external stimulus can reversibly tune the wavelength and/or the amplitude of the LSPR, are the subject of important research efforts because of their potential for writing, reading,

storing and processing information at the nanoscale. The easiest way to obtain such active plasmonic devices consists in surrounding NPs with switchable materials where an external input changes their effective dielectric constant. Several external stimuli have already been employed, based on thermo-, [1–3] pH-, [4] photo-, [5,6] electrical-[7] and redox-responsive [8–16] materials, these stimuli allowing to change the phase, [1,2,5–7] the spin [3] or the conductivity [9,14–16] of the material.

In particular, electrochemically driven active plasmonic devices have been studied by using conducting polymers as the surrounding media: polyaniline (PANI), [9,15] poly(3,4-ethylenedioxythiophene) (PEDOT) [14,15] or polythiophene [16] and bithienyl-based oligomers covalently attached to electrodes *via* a benzene spacer [16]. Indeed, conducting polymers and oligomers can switch from a reduced insulating state to an oxidized conducting state depending on their doping level, [17] leading to a change of their dielectric constant [18,19]. The effect on the LSPR depends on the size and the shape of the NPs, and on the nature and the thickness of the conducting polymer film deposited on them. The LSPR can be either shifted or damped. For example, a giant blue-shift of 192 nm is observed for a PEDOT film about 150 nm-thick deposited onto prolate AuNPs (around 120–140 nm in diameter), when it is switched from its reduced nonconducting

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state to its oxidized conducting state, the effect on the amplitude of the LSPR being insignificant [14]. On the contrary, the LSPR is completely damped when a PANI film around 100 nm-thick, deposited onto prolate AuNPs, is oxidized to its conducting state [12]. The LSPR can be modulated by thinner films, but the thinner the organic film, the smaller the effect [13,16].

To generate such electroactive plasmonic devices, NPs should be deposited on conducting transparent materials, in order to allow the electrochemical switch and the study of the LSPR signal. For this reason, transparent indium-tin oxide (ITO) electrodes have been chosen as substrates. The classical method of fabricating arrays of well ordered NPs of regular size and controlled shape on ITO electrodes uses electron-beam (e-beam) lithography [9,11,12,14,16]. Unfortunately, this technique generates very small arrays, typically around 100 μm -wide, since the process is so slow. Moreover, this method is expensive because it requires a scanning electron microscope and a metal evaporation apparatus. In this context, there is a strong need to develop a low-cost technique to obtain large-area AuNP plasmonic substrates, with good LSPR characteristics.

One of the easiest and cheapest method of making plasmonic electrodes relies on the synthesis of AuNPs from an Au^{III} salt by electrochemical reduction. This method has rarely been used on transparent electrodes [20,21], and in these cases, the LSPR of the AuNP-modified electrodes was not easily controlled and was not close to that obtained when e-beam deposition is used. Note also that vapor phase gold deposition, through a template generated using nanospheres of various diameters, has also been used to generate cheap plasmonic electrodes [22–24]. Different template-free methods have been also used to functionalize surfaces with gold nanoparticles [25–27].

In this work, we describe a method to fabricate AuNP plasmonic substrates with good optical response, using a template- and surfactant-free electrosynthesis process. The LSPR of such plasmonic electrodes will be compared with that of e-beam lithographic gratings, and the effect of the electrodeposition parameters on the shape, the size and the dispersity of the AuNPs, and consequently on the LSPR, is discussed. These substrates will be used to generate active plasmonic devices by covering the AuNPs with an ultrathin organic film of bithienylbenzene (BTB). The effect of the conductance switch of this ultrathin electroactive organic layer on the properties of AuNPs is reported.

2. Experimental

2.1. Chemical reagents

Potassium gold(III) chloride (KAuCl_4) and sodium carbonate (Na_2CO_3), purchased from Sigma-Aldrich, were used as supplied. ITO-coated glass plates with a square resistance of 30–50 Ω /square were purchased from Solems.

All aqueous solutions were freshly prepared using ultrapure water (18.2 $\text{M}\Omega\text{ cm}^{-1}$) obtained by passage through a Milli-RO unit and subsequently through a Milli-Q water purification set.

2.2. Materials

A CHI 600°C electrochemical workstation (CH instruments) was employed in all electrochemical experiments, which were carried out with a conventional one-compartment three-electrode cell. The reference was a saturated calomel electrode (SCE) and the counter-electrode a stainless steel grid. A Zeiss Supra 40 scanning electron microscope was used to evaluate the shape and size of AuNPs. The LSPR of AuNPs was recorded using an Ocean Optics HR4000 UV–visible spectrophotometer. Free-ITO area and BTB-

covered ITO area were used as references to record spectra of AuNP and BTB/AuNP devices, respectively. To make LSPR measurements under electrochemical control, a home-made planar three-electrode cell with a stainless steel grid counter-electrode and a silver (Ag/AgCl) pseudo-reference electrode was used.

2.3. Electrosynthesis of gold nanoparticles

ITO electrodes were cleaned by sonication for 20 minutes in dilute alkaline Extran[®] solution (Merck), then carefully rinsed with distilled water and then ethanol; they were stored in ultrapure Milli-Q water until required for AuNP electrodeposition.

Electrodeposition experiments were carried out by the chronoamperometry technique in a stirred aqueous solution of 2.10^{-3} M KAuCl_4 and 0.25 M Na_2CO_3 . The solution was maintained under argon atmosphere during the whole experiment. AuNPs were deposited on clean ITO electrodes at a constant potential and a controlled total charge current density of 20 mC cm^{-2} .

2.4. Bithienylbenzene (BTB) diazonium grafting

1-(2-Bisthienyl)-4-aminobenzene (BTAB) was synthesized as previously described [28]. Grafting onto substrates was performed using *in situ* diazonium salt formation: under argon 30 eq. of *tert*-butyl nitrite were added to a 0.5 mM solution of BTAB in acetonitrile containing 0.1 M of tetra-*n*-butylammonium tetrafluoroborate (TBABF_4). BTB was grafted by multi-scan cyclic voltammetry (CV) (15 successive cycles) in the cathodic range (between 0.3 and -0.5 V/SCE) at a scan rate of 100 mV/s . By this means, films less than 15 nm-thick are generated. A full description of the BTB thickness measurements on gold gratings generated by e-beam can be found in a previous publication [16].

3. Results and discussion

3.1. Electrodeposition of AuNPs onto ITO electrodes

AuNP substrates were obtained by electrochemical reduction of KAuCl_4 in an aqueous solution containing Na_2CO_3 as supporting electrolyte. Chronoamperometry was used at various potentials, the total charge density (in mC cm^{-2}) used during the reduction process being fixed by adjusting the deposition time for each experiment and monitoring the charge flowing. Several charge densities were used but the best results were obtained when it was fixed at 20 mC cm^{-2} . Fig. 1 shows the optical extinction spectra of five large-area AuNP substrates obtained at different reduction

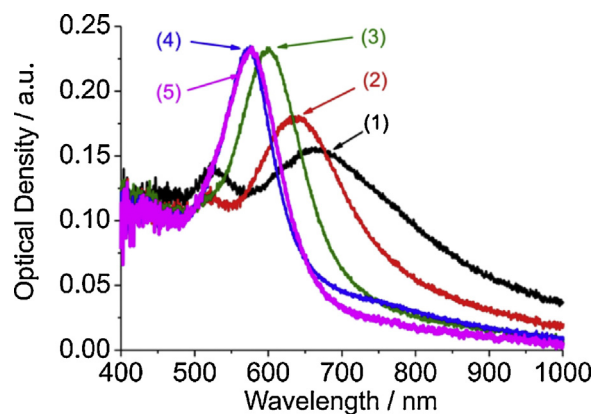


Fig. 1. Optical extinction spectra of AuNPs on ITO electrodes obtained at various reduction potentials (-0.6 to -1.0 V/SCE) and with a total deposited charge density $Q = 20\text{ mC cm}^{-2}$. (1) deposition at -0.6 V , (2) at -0.7 V , (3) at -0.8 V , (4) at -0.9 V , (5) at -1 V/SCE .

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