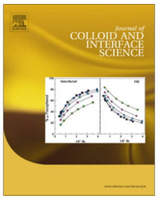
Journal of Colloid and Interface Science 410 (2013) 1–10

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis



Editor's Choice

Ordered gold nanoparticle arrays on glass and their characterization

Jie Yuan [a,b], Akram Hajebifard [c], Christeen George [a,b], Pierre Berini [c,d,*], Shan Zou [a,*]

[a] National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada
[b] Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur, Ottawa, Ontario K1N 6N5, Canada
[c] Department of Physics, University of Ottawa, 150 Louis Pasteur, Ottawa, Ontario K1N 6N5, Canada
[d] School of Electrical Engineering and Computer Science, University of Ottawa, 800 King Edward, Ottawa, Ontario K1N 6N5, Canada

ARTICLE INFO

Article history:
Received 16 May 2013
Accepted 29 July 2013
Available online 12 August 2013

Keywords:
Gold nanoparticles (AuNPs)
Localized surface plasmon resonance (LSPR)
Self-assembly
Diblock copolymer
Seeding growth

ABSTRACT

Using self-assembly of block copolymer micelle loaded metal precursors, combined with a seeding growth route, we have developed a novel approach to create ordered metal nanoparticle (NP) arrays of controllable size over large areas (~80 mm^2) on solid substrates. Atomic force microscopy (AFM), UV–Vis extinction spectrophotometry, and theoretical simulations were systematically carried out to determine the size and pattern of NP arrays, and locate the localized surface plasmon resonance (LSPR) peak. By tuning the molar ratios of precursors, hexagonal arrays of AuNPs of mean heights of 5.2 ± 0.6 nm, 8.3 ± 1.7 nm, and 10.0 ± 2.1 nm were obtained by self-assembly of poly(styrene-*b*-2-vinyl pyridine) micelle-loaded gold salt on glass. Further seeding growth was then used to enlarge the AuNPs to heights of 25.7 and 33 nm and decrease the edge-to-edge inter-particle spacing. The optical response of AuNP arrays was determined by measuring and computing their absorbance spectra as a function of the cover medium refractive index over the range from 1 to 1.55; the measured spectra agree very well with the computations. The resonance wavelength red-shifts as the medium refractive index increases and the bulk sensitivity of the arrays increases with increasing AuNP size. When the edge-to-edge inter-particle spacing decreased to ~50 nm, coupling of adjacent AuNPs became apparent, as a shoulder which developed in the spectra. Also, the AuNPs were found to be embedded in the substrate glass by about ~20–30%, as determined by comparing the experimental and computed bulk sensitivities. The fabrication technique devised is suitable for low-cost mass-manufacturing of large area arrays of ordered high-quality AuNPs on a substrate for biosensor or other applications.

1. Introduction

The unique chemical, optical and electro-kinetic properties of gold nanoparticles (AuNPs), which are size- and shape-dependent, have been widely used in catalysts, solar energy harvesting, and sensing applications [1–5]. Although e-beam lithography or focused ion beam milling are commonly used to fabricate metallic nano-structures, the serial nature of these processes and their high costs are limiting. There is a pressing need for controlled solution-based nanoparticle fabrication methods applicable to large-area samples or substrates. Efforts have been expended in this direction but it remains challenging to create ordered metal NP arrays of controlled particle size and controlled spacing between particles. Using alkyl chain length (ligand-) controlled AuNP spacing, Lin and others have demonstrated the possibility to prepare AuNP super-lattices by controlling solvent evaporation [6–8]. However, this approach limits the spacing of AuNPs to ~3 nm due to difficulties in the synthesis of longer alkyl chain lengths [9]. DNA-based routes extended the AuNP spacing to 20 nm [10–16], but unfortunately, it is difficult to produce a continuous super-lattice sheet of AuNPs over a large area [12,16]. Möller et al. introduced the method of using diblock copolymer micelles to load metal precursors and form NP arrays on solid supports [17]. For example, $AuCl_4^-$ ions bind tightly to protonated pyridine units in the core of micelles so that the micelle structure served as nanoreactors and carriers of AuNPs [4,17–26]. This solution-based approach can yield NPs of uniform size (narrow size distribution), and is a simple and cost-friendly NP fabrication method [18,23,27].

Localized surface plasmon resonances (LSPRs) are charge density oscillations on metal NPs excited by light. They are sensitive to the optical properties of the surrounding environment. Metal NPs can scatter or absorb incident light. Extinction, the summation of absorption and scattering, is an optical property that characterizes metal NPs, particularly extinction spectra which reveal the location of LSPRs. According to the Mie theory [28], for metal NPs with a

---

[*] Corresponding authors at: School of Electrical Engineering and Computer Science, University of Ottawa, 800 King Edward, Ottawa, Ontario K1N 6N5, Canada. (P. Berini), National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada (S. Zuo).

E-mail addresses: berini@eecs.uottawa.ca (P. Berini), shan.zou@nrc-cnrc.gc.ca (S. Zou).

0021-9797/$ - see front matter Crown Copyright © 2013 Published by Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.07.070

diameter much smaller than the exciting wavelength, the extinction, absorption and scattering cross-sections are given by [29]

$$c_{ext} = c_{abs} + c_{scat} \tag{1}$$

$$c_{abs} = k\mathrm{Im}(\alpha) = 4\pi R^3 \left(\frac{2\pi}{\lambda_0}\right)\left(\frac{3\varepsilon_2\varepsilon_d^{3/2}}{|\varepsilon_1 + 2\varepsilon_d|^2 + \varepsilon_2^2}\right) \tag{2}$$

$$C_{scat} = \frac{1}{6\pi}k^4|\alpha|^2 = \frac{8\pi R^6}{3}\left(\frac{2\pi}{\lambda_0}\right)^4 \varepsilon_d^2\left(\frac{|\varepsilon_1 - \varepsilon_d|^2 + \varepsilon_2^2}{|\varepsilon_1 + 2\varepsilon_d|^2 + \varepsilon_2^2}\right) \tag{3}$$

$$\alpha = 4\pi R^3\left(\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}\right) \tag{4}$$

where k is the wavenumber of the incident light, λ_0 is the free-space wavelength, R is the radius of the nanoparticle, ε_d is the dielectric constant of the surrounding medium, and $\varepsilon_m = \varepsilon_1 + i\varepsilon_2$ is the dielectric constant of the metal ($e^{-j\,\omega\,t}$ time-harmonic form implied). For a good plasmonic metal ($\varepsilon_2 \ll \varepsilon_1$) the extinction is largest at the wavelength where $\varepsilon_1 = -2\varepsilon_d, k = 2\pi\sqrt{\varepsilon_d}/\lambda_0$ for the case of the dipolar (bright) LSPR; we denote this wavelength as λ_{LSPR}. While λ_{LSPR} is mainly determined by the real part of the metal dielectric constant, the strength and width of theextinction, absorption and scattering spectra are determined mainly by the imaginary part of the dielectric constant, see Eqs. (1)–(3). For small NPs of diameter in the range of 10–30 nm, absorption dominates [30,31].

Several key factors are essential in characterizing metal NP arrays. First of all, λ_{LSPR} depends on the refractive index of the NP's surrounding medium, including the substrate, cover medium and any adsorbed species [1,3,32–39]. Secondly, when two or several AuNPs are deposited closely enough, inter-particle coupling is not negligible [40–46]. Depending on the orientation of AuNP arrays, the LSPR is polarization sensitive, and both red-shifts and blue-shifts can be achieved with increasing cover index [42]. Lastly, bandstructure effects can become more prevalent in the optical properties of AuNPs if they can be organized on the atomic scale [47]. In general, most of these characteristics can be enhanced significantly and utilized effectively if the AuNPs are organized in accurate and organized arrays [48].

Here, we report a simple fabrication method to generate hexagonal ordered AuNP arrays on glass cover slip substrates using self-assembly combined with seeding growth approach. As shown in Scheme 1, hexagonal patterned gold salt loaded poly(styrene-*b*-2-vinyl pyridine) (PS-*b*-P2VP) micelles are spin-coated on substrates, and the polymer shell is removed by oxygen plasma etching. Arrays of AuNPs with 5 to 10 nm in size were created on glass substrates forming "seeds", from which larger AuNPs were grown chemically. Series of AuNP sizes with controlled inter-particle spacing were obtained over large areas on glass substrates. The absorbance spectra of AuNP arrays on glass were characterized by UV–Vis spectroscopy. The influence of size, inter-particle spacing, surrounding permittivity (substrate and cover medium), and AuNP embedding ratio into the substrate are discussed. Also, the influence of the ionic strength and charge density of the micelle solution were considered.

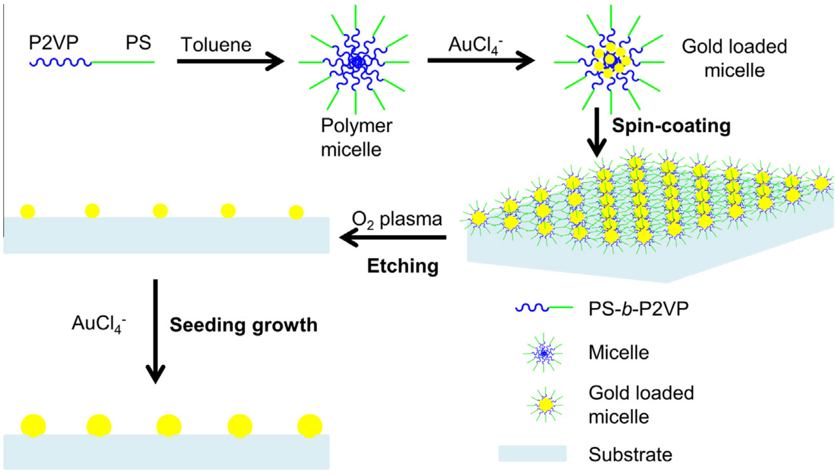
2. Materials and methods

2.1. Chemicals

Diblock copolymer poly(styrene(48.5k)-*b*-2-vinyl pyridine(70k)) (PS-*b*-P2VP, Polymer Source Inc., Montreal, QC, Canada) was used as purchased. Gold(III) chloride hydrate (99.999%) ($HAuCl_4$) and hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) were both purchased from Sigma–Aldrich Canada Ltd. (Oakville, ON, Canada), and used as received. 25 mm (78.5 mm^2) premium glass cover slip substrates were purchased from Fisher Scientific (Ottawa, ON, Canada). 45 × 12.5 × 3.5 mm^3 quartz cuvettes were purchased from Hellma Canada Ltd. (Concord, ON, Canada). HPLC grade methanol, dichloromethane, heptane, 99% ethanol, chloroform and *o*-dichlorobenze were purchased from EMD Chemicals Inc. (Gibbstown, NJ, USA), Greenfield Ethanol Inc. (Brampton, ON, Canada), Caledon Laboratories Ltd. (Georgetown, ON, Canada) and Sigma–Aldrich Inc. (St. Louis, MO, USA). ACS grade toluene (Fisher Scientific, Fair Lawn, NJ, USA) was purified using an Innovative Technology Pure Solv. Device (activated alumina column containing a copper catalyst and molecular sieves). Milli-Q water deionized to a resistivity of 18 MΩ cm was used in all of the experiments.

2.2. Combined self-assembly and seeding growth methods

Patterned AuNP arrays on glass cover slips were prepared by the self-assembly of diblock copolymer micelle loaded gold salt [17,25,26,48,49]. Briefly, 5 mg/mL diblock copolymer micelle solution was prepared in dry toluene by vigorous stirring. Gold precursor ($HAuCl_4$) was added to the micelle solution at a molar ratio of 0.1, 0.2, 0.3, 0.4 and 0.5 per pyridine unit. The gold loaded micelle



Scheme 1. Processes of forming ordered hexagonal AuNP arrays on glass substrates: combining the self-assembly of diblock copolymer micelle loaded gold precursors with the seeding growth method.