Published in final edited form as:

Electrochem commun. 2009 October ; 11(10): 1964–1967. doi:10.1016/j.elecom.2009.08.029.

REAL-TIME PROBING OF THE GROWTH DYNAMICS OF NANOPARTICLES USING POTENTIOMETRIC ION-SELECTIVE ELECTRODES

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Abstract

This Communication demonstrates the ability of potentiometric ion-selective electrodes (ISE) to probe the growth dynamics of metal nanoparticles in real-time. The new monitoring capability is illustrated using a solid-contact silver ISE for monitoring the hydroquinone-induced precipitation of silver on gold nanoparticle seeds. Potential-time recordings obtained under different conditions are used to monitor the depletion of the silver ion during the nanoparticle formation and shed useful insights into the growth dynamics of the nanoparticles. Such potentiometric profiles correlate well with the analogous optical measurements. The new real-time electrochemical probing of the particle growth process reflects the direct, rapid and sensitive response of modern ISE to changes in the level of the precipitated metal ion from the bulk solution and holds considerable promise for probing the preparation of different nanoscale materials.

Keywords

Nanoparticles; Growth; Ion-selective electrodes; Potentiometry; Silver; Hydroquinone

1. Introduction

The considerable interest in nanomaterials is driven by their many desirable properties, particularly the ability to tailor the size and structure and hence the properties of nanomaterials [1–3]. Accordingly, new and improved methods for characterizing the formation of nanomaterials are highly desired. Most commonly, the growth of metal nanoparticles is accomplished using optical methods such as UV-vis [4], photoluminescence [5], or microscopy techniques such as transmission electron microscopy [6] or scanning electron microscopy [7]. However, those techniques require bulky and expensive instrumentation, as well as specially-trained operators to perform the measurements. Surprisingly, electrochemical techniques have not been used for direct monitoring of nanoparticle formation processes.

Here we demonstrate for the first time that potentiometric ion-selective electrodes (ISEs) are attractive tools for the direct and continuous monitoring of nanoparticle growth. Electrochemical techniques are advantageous for in-situ monitoring applications due to their rapid response, inherent miniaturization, low cost and independence of sample turbidity. Electrochemical devices such as pH or oxygen electrodes have been widely used for continuous real-time industrial or environmental monitoring [8]. Recent advances in direct potentiometry

[9–11] have led to powerful ISE sensing devices, with remarkable selectivity and sensitivity (down to the sub-nanomolar level), fast and reversible response and hence a powerful monitoring capability. We demonstrate here that such advanced potentiometric microsensors are very attractive for probing in real-time the growth and formation of nanoscale materials. The new monitoring capability is illustrated using a solid-state silver ISE in connection to the common hydroquinone-induced precipitation of silver on gold nanoparticle seeds. By offering a fast return of the chemical information regarding the level of solute ions such continuous and direct potentiometric monitoring shed useful insights into the growth kinetics of nanoscale materials and is expected to extend and complement the arsenal of techniques available for probing the dynamics of nanoparticle formation.

2. Experimental

2.1 Chemicals

Hydroquinone, gold nanoparticles (10 nm diameter, 0.01% HAuCl₄, G1527) and silver nitrate salt were purchased from Sigma-Aldrich (St. Louis, MO). The ionophores *o*-xylylenebis (*N,N*-diisobutyldithio-carbamate) (copper(II) ionophore (I)), sodium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (Na-TFPB) and lipophilic salt tetradodecylammonium tetrakis (4-chlorophenyl)-borate (ETH 500) were purchased in Selectophore® or puriss grade from Fluka (Buchs, Switzerland). The solvent methylene chloride was obtained from Fisher (Pittsburgh, PA), poly(3-octylthiophene) (POT) was synthesized following the procedure of Jarvinen et. al [12] and purified according to the patent application [13]. The synthesis of methyl methacrylate-decyl methacrylate (MMA-DMA) copolymer matrix was accomplished as described previously [14]. All stock and buffer solutions were prepared using double-deionized water (18.2 MΩ cm).

2.2 Membranes

The membrane for the Ag-ISE was prepared by dissolving 50 mg of components in 0.8 mL of methylene chloride: copper (II) ionophore (I) (17 mmol/kg), Na-TFPB (7 mmol/kg), ETH 500 (12 mmol/kg), and MMA-DMA. The membrane cocktail was degassed by sonication for 1 min prior to use for coating the microelectrodes.

2.3 Microelectrode

The solid-contact Ag-ISE was prepared by using a 2 cm long gold wire (200 μm diam.) that was soldered to a copper wire for electric contact. Before use the gold wires were thoroughly cleaned with diluted sulfuric acid, and rinsed with water, then acetone and left for 3 min in chloroform. The POT solution (25 mM of the respective monomer) was applied along the length of the gold wire at least three times until the color of the wire became black. After the gold wires were fully covered with POT they were allowed to dry. Then, the wires were inserted into a 10-μL polypropylene pipette tip so that they were level with the end of the micropipette tip. Finally, the membrane 'cocktail' was drop cast to the tip of the POT-coated wire for three times at 15 minute-intervals and left to dry for at least 1 hour. The resulting microelectrodes were conditioned prior to use for one day in a 10⁻³ M AgNO₃ solution, followed by another day in a 10⁻⁷ M AgNO₃.

2.4 Apparatus

Potentiometric measurements were performed with a multifunctional data acquisition board (779026-01 USB-6009 14 Bit, National Instruments, Austin, TX) connected to a six-channel high Z interface (WPI, Sarasota, FL). Optical measurements were performed using the LAM BDA 35 spectrophotometer purchased from Perkin-Elmer (Waltham, MA).

2.5 Measurements

Potentiometric measurements were carried out in a 2 mL sample using the solid-contact Ag ISE and a commercial Ag/AgCl double junction electrode as reference (Type 6.0729.100, Metrohm AG, 9101 Herisau, Switzerland). To avoid contamination of the sample, LiCH_3COO was used as the bridge electrolyte. The bridge tip had an outer diameter of 4 mm. All potentiometric measurements were performed at room temperature using deionized water as the background medium. Activity coefficients for silver were calculated according to the Debye-Huckel approximation and the potential values were corrected for liquid-junction potentials with the Henderson equation.

Spectrophotometric measurements were also performed at room temperature in a 2 mL quartz cuvette with a 1 cm length path, with repetitive spectra recorded every 10 s.

3. Results and Discussion

We demonstrate here that ion-selective electrodes (ISE) are very attractive tools for the direct monitoring of nanoparticle growth. To illustrate this monitoring capability we selected the common hydroquinone-induced precipitation of silver on gold nanoparticle seeds [15] and probed the progress of this reaction using a solid-contact Ag^+ ISE [11]. The reaction between hydroquinone and silver ions, also known as silver enhancement, has been widely used in histochemical microscopy studies [15], in connection to gold nanoparticle seeds acting as catalysts to reduce silver ions to metallic silver. The autometallographic silver deposition procedure enlarges the size and darkens the color of the gold particles [16], while liberating a quinone product.

The solid-contact silver ISE was first characterized in a silver calibration experiment, where it displayed good linearity (E vs. $\log [\text{Ag}^+]$) over a wide concentration range between 10^{-9} and 10^{-3} M silver, with a slope of 58.8 mV/decade, along with a low detection limit of 2×10^{-9} M (not shown). Subsequently, the silver sensor was applied for monitoring the hydroquinone-stimulated precipitation of silver on gold nanoparticles.

Figure 1 demonstrates the ability of the silver ISE to probe the progress of the hydroquinone-induced silver reduction in the presence of gold nanoparticle seeds. This figure displays potentiometric potential-time traces obtained at the Ag^+ ISE in the presence of 10^{-3} M silver ion and different levels of hydroquinone: 5×10^{-3} (a), 1.25×10^{-3} (b), 1×10^{-3} (c), 7.5×10^{-4} (d) and 5×10^{-4} M (e). The ISE allows real-time monitoring of the silver precipitation process, as it responds continuously and instantaneously to the changes in the level of the silver ions. Decreasing potentiometric signals are thus observed upon adding the hydroquinone, reflecting the decreasing concentration of the silver ion. Such potential-time profiles reflect the different growth kinetics in the presence of different levels of hydroquinone. As expected, faster reactions (indicated from the sharper potential change) are observed upon increasing the hydroquinone concentration (i.e., for faster silver depletion). The direct potential readout actually allows for a real-time estimate of the level of silver ion remaining in the solution. For example, the times required for reducing 90% of the silver ions at hydroquinone concentrations of 5×10^{-3} , 1.5×10^{-3} , 1×10^{-3} , 7.5×10^{-4} and 5×10^{-4} M correspond to 3, 7, 17, 26 and 33 minutes, respectively (based on the 59 mV potential change per 10-fold concentration decrease). The potential is stabilized after longer times (at ~ 340 mV) for the different hydroquinone concentrations. The overall potential change (of ca. 120 mV, i.e., two concentration decades) observed during these reactions indicates that the equilibrium state correspond to the reduction of 99% of the silver ion (independent of the hydroquinone concentration). Apparently, not all the silver is consumed, even in the presence of a large (5-fold) excess of hydroquinone (plot a). Since the signal output of the ISE corresponds to the logarithm of the concentration (strictly, activity) of the solute ion, such direct potentiometric

monitoring of the depleted metal ion provides additional (and unique) information on the formation of nanoparticles, which is not accessible by other techniques. For example, Figure 1 indicates a two-step growth process over the silver concentration ranges from 10^{-3} to 10^{-4} and 10^{-4} to 10^{-5} M, that may account for different phases of the particle formation. Parallel spectrophotometric observation of the growth process did not suggest significant particle size heterogeneity, with a well defined band appearing at 403 nm in complete analogy to earlier work [17]. It is not fully clear at this stage which growth mechanisms are responsible for the potential changes observed in Figure 1. These may include nucleation and autocatalytic growth or a late stage growth mechanism. One can argue that the steps observed in Figure 1 are not due to nucleation and growth, but rather reflect varying kinetics in the later stages of nanoparticle growth (that are due to size of the particles). Such argument is attributed to the fact that nucleation will be difficult to see with ISEs since it occurs at a stage where the bulk silver concentration is not yet changing perceptibly. Such monitoring of the hydroquinone-induced silver reduction is accomplished by adding together the Ag ions along with the gold nanoparticles (Figure 1). Non-specific adsorption of the silver ions onto the gold surface can be distinguished and detected separately by adding the gold nanoparticles into the silver-ion solution.

Figure 2A presents the time-dependent consumption of silver ions by hydroquinone, with the activity estimated (i.e., using the anti-log domain), in accordance to the Nernst equation based on the E-t profiles of Figure 1. Note that the same equilibrium is reached for the three different hydroquinone concentrations [5(a), 1(b) and 0.5(c) mM]. As was illustrated earlier, the decrease of silver ions can be correlated to the nanoparticle growth kinetics, which is illustrated in Figure 2B (obtained by inverting Figure 2A) using the percentage of the silver nanoparticles formed as displayed values.

These ISE growth profiles were correlated with those obtained by a common optical (UV) method [19] (Figure 2, B vs. C). Such correlation is possible since the response obtained with the common spectrophotometric technique (Figure 2C) displays a similar shape and temporal profile as the one obtained with the Ag-ISE. The spectrophotometric measurements were performed under similar conditions used for potentiometric measurements, in connection to a wavelength of 403 nm, which is characteristic for Ag-nanoparticles [17]. Note that such optical probing is susceptible to various limitations, such as overlapping signals [18] or limited resolution [19]. The new potentiometric technique, in contrast, offers an attractive alternative to such spectrophotometric probing, where the consumption of the solute ion during the nanoparticle growth is monitored and can yield a highly useful complementary information.

We examined the influence of other variables of the gold-promoted silver reduction, including the influence of the levels of the silver or gold ions. For example, Figure 3 displays potential-time profiles recorded at the Ag^+ ISE in the presence of different concentrations of silver ion: 1 (A), 0.1 (B) and 0.01 mM (C). As expected, the initial potential value increases with the silver ion concentration. However, adding the same (1 mM) hydroquinone concentration results in a faster yet smaller potential change in the presence of the lower silver concentration, with equilibrium reaching within less than 5 min (C). Note, in contrast, the slow reaction observed in the presence of 1 mM silver where equilibrium is not reached even after 25 min (A). The potential changes observed in the presence of 0.10, 0.1 and 1.0 mM Ag(I) – 45, 90 and 75 mV, respectively – correspond to the depletion of 85, 95, and 97 % of this solute ion. Similarly, we tested different volumes (10, 20 and 50 μL) of the commercial gold nanoparticles (catalytic seed) solution. We observed the largest catalytic effect (potential change) using the 50 μL gold solution and the slowest reaction using a 10 μL gold solution (not shown).

4. Conclusions

This communication has illustrated for the first time the use of ISEs for probing the growth of nanoparticles in real-time. Such monitoring of the growth kinetics of nanoparticles is possible because of the rapid, direct, continuous and sensitive potential response of modern ISEs to changes of solute ions. The silver ISE has been shown to be particularly useful for gaining information about the kinetic processes at later stages of nanoparticle growth, in which case the solute ions become dilute and concentration changes are much more easily discerned compared to other methods. The corresponding potentiometric growth profiles correlate otherwise well with analogous optical measurements. While the concept has been documented in connection to the hydroquinone-induced formation of silver nanoparticles it could be readily expanded to the formation of other nanoscale structures using different ISE microsensors.

Acknowledgments

Financial support from the National Institutes of Health (RO1 EB002189) and the National Science Foundation (CHE 0506529) is gratefully acknowledged.

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Figure 1. Potential trace lines recorded at the Ag ISE during the hydroquinone-induced precipitation of silver onto gold nanoparticle seeds. Conditions: AgNO_3 (10^{-3} M), gold nanoparticles (10 nm; 50 μL) and different hydroquinone concentrations: a) 5×10^{-3} M, b) 1.25×10^{-3} M c) 1×10^{-3} M, d) 7.5×10^{-4} M and e) 5×10^{-4} M.

Figure 2.

A) Concentration profiles reflecting the consumption of silver ions after reacting with hydroquinone solution. B) Decrease in the percentage of silver ions using a μ ISE. C) Spectrophotometric measurements for the formation of silver particles on the gold nanoparticles. Hydroquinone concentrations: a) 5×10^{-3} M, b) 1×10^{-3} M and c) 5×10^{-4} M.

Figure 3. Effect of the Ag(I) concentration upon the hydroquinone-induced precipitation of silver onto gold nanoparticle seeds. Potential trace lines recorded at the Ag ISE during the nanoparticle growth using Ag(I) levels of: A) 1 mM; B) 0.1 mM; C) 0.01 mM. Other conditions, as in Figure 1.