

Dithiocarbamate-Capped Silver Nanoparticles

Moony C. Tong, Wei Chen, Jia Sun, Debraj Ghosh, and Shaowei Chen*

Department of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, California 95064

Received: May 22, 2006; In Final Form: August 1, 2006

Nanometer-sized silver particles were synthesized by using didecylamine dithiocarbamates as the protecting ligands. With control of the initial ligand–metal feed ratios, the core diameter of the resulting particles was found to vary from about 5 to 2.5 nm, as determined by transmission electron microscopic measurements. The core size dispersity was also found to decrease with increasing feed ratio. In UV–visible spectroscopic studies, the particle surface plasmon resonance peak diminished in intensity as the particle core size decreased, whereas in electrochemical measurements, smaller sized particles gave rise to well-defined quantized charging voltammetric features, in contrast to the featureless responses with the larger particles. Such single electron-transfer behaviors were consistent with those observed in STM measurements involving individual nanoparticles. Overall, this study provides an effective approach to the synthesis of stable nanometer-sized silver nanoparticles with interesting electronic and electrochemical properties.

Introduction

The controlled synthesis of nanometer-sized particles has been challenging and yet of immense fundamental and technological significance because of their diverse potential applications, in particular, in the areas of nanoelectronics and nanocircuitries.^{1,2} For instance, nanoparticles have been explored as the effective structural elements for the bottom-up fabrication of novel electronic nanodevices by exploiting their single-electron transfer (SET) properties (i.e., Coulomb Staircase).³ The fundamental basis for SET is that the energetic barrier for a single-electron transfer ($e^2/2C_{\text{MPC}}$, with e being the electronic charge and C_{MPC} the particle molecular capacitance) is substantially greater than the thermal kinetic energy (kT). This renders it necessary to limit the particle dimension to the nanometer regime and the particle molecular capacitance of the order of attofarad (aF). This is typically achieved by the passivation of the nanoparticle surface by a low-dielectric capping layer.

While the SET phenomena are traditionally observed by scanning probe microscopic measurements,⁴ the availability of monodisperse nanosized particles also renders it possible to achieve the same behaviors in solution-phase electrochemistry.⁵ So far, most electrochemical studies of nanoparticle single-electron transfer (or quantized capacitance charging) are focused on gold nanoparticles, partly because of the chemical stability of the particles and the relative ease in the preparation of particles with core size in the nanometer range.^{5,6} More recently, similar behaviors are observed with nanoparticles of several other transition metals, such as Pd,^{7–9} Cu,¹⁰ and Ru.¹¹ However, while there have been a few reports claiming the observation of electrochemical quantized charging with Ag nanoparticles,^{12–14} the related studies are not very conclusive. Thus, in this report, our major goal is to develop an effective protocol for the synthesis of nanometer-sized Ag nanoparticles, especially with diameter smaller than 3 nm, and to demonstrate that these particles exhibit well-defined quantized charging characters in electrochemical and STM measurements at ambient temperature.

It should be noted that there have been numerous reports on the synthesis of monolayer-protected Ag nanoparticles.^{15–17} However, in most of these studies the particle core diameter is too large (>3 nm) to observe the electrochemical quantized charging features. In fact, this is one of the challenges with Period V metals as compared to those in Period VI, partly because of the weaker metal–metal bonding interactions and less tolerance of structural defects, and consequently relatively larger particle core dimensions.⁷ It has been proposed that the particle growth dynamics can be approximated as the combined consequence of two competing processes, nucleation of zero-valence metal atoms forming cluster cores and passivation of the clusters by surface-protecting ligands.¹⁸ Thus, one can envision that the choice of appropriate surface-capping ligands is critical in the control of the eventual particle structures. While alkanethiols have been conventionally used as the ligands of choice as first demonstrated by Brust et al.,¹⁹ more recently, other mercapto derivatives have been used as well, most of which are limited to the synthesis of Au particles.^{20–22} Because of the bidentate nature of the dithiocarbamate (DTC) ligands, it is anticipated that they will exhibit stronger affinity to the metal surface than simple alkanethiols and hence smaller particle cores.^{20,21}

In this report, DTC derivatives are used as the capping ligands to stabilize silver nanoparticles. The average particle core diameter can be controlled within the range of 2.5–5 nm by the initial feed ratio of DTC and silver salt concentration. Electrochemical measurements of the smaller sized particles exhibit interesting SET features consistent with those in STM studies.

Experimental Section

Chemicals. Carbon disulfide (CS₂, Fisher Scientific, spectroanalyzed), didecylamine (98%, Aldrich), silver nitrate (AgNO₃, Fisher), superhydride (LiB(C₂H₅)₃H, 1 M in THF, ACROS), and tetrabutylammonium perchlorate (TBAP, 98%, ACROS) were used as received. All solvents were obtained from typical commercial sources and were used without further

* To whom correspondence should be addressed. E-mail: schen@chemistry.ucsc.edu.

treatment. Water was supplied by a Barnstead Nanopure water system (18.3 M Ω).

Synthesis of DTC-Capped Silver Nanoparticles. Didecylamine dithiocarbamate (DTC10) was first synthesized by following a literature protocol.²¹ Briefly, carbon disulfide (CS₂) was first dissolved in ethanol at a concentration of 10%; a separate solution with the stoichiometric amount of didecylamine was also prepared in ethanol. The amine portion was added dropwise to the CS₂ solution, and the resulting mixture underwent vigorous stirring for 30 s, leading to the facile synthesis of didecylamine dithiocarbamate (DTC10), which would then be used for the synthesis of silver nanoparticles.

In a typical synthesis of silver nanoparticles, 0.5 mmol of silver nitrate was first dissolved in 2 mL of ethanol, to which was added 20 mL of toluene. A calculated amount of the DTC10 ligands synthesized above was then added dropwise into the AgNO₃ solution which yielded a bright green color, most likely because of the formation of Ag(I)–DTC complexes. Upon the addition of superhydride (5 mmol), the solution immediately turned dark black, signifying the formation of Ag nanoparticles. The solution was under magnetic bar stirring for at least 3 h before the toluene phase was collected, dried in a rotary evaporator, and purified by extensive rinsing on a glass frit with copious ethanol and acetone to remove excessive DTC ligands (as attested in ¹H NMR measurements), similar to the processing procedure for Au nanoparticles.²³ The resulting particles were found to be soluble in apolar solvents such as alkanes, toluene, dichloromethane, THF, and so forth, but not in polar solvents such as alcohols, acetone, and acetonitrile. Three samples of dithiocarbamate-capped silver nanoparticles were prepared with the initial molar ratio of DTC to silver varying from 0.5 to 1 and 1.5. The resulting particles were then denoted as AgDTC (0.5 \times), (1 \times), and (1.5 \times), respectively.

Spectroscopies. The particle purity was examined by using ¹H NMR spectroscopy (Varian Unity 500 MHz) with a concentrated solution of particles dissolved in CDCl₃. In TEM measurements, the samples were prepared by casting a drop of the particle solution in dichloromethane onto a 200-mesh carbon-coated copper grid; and at least three images were acquired for each sample with a JEOL 1200 EX transmission electron microscope (TEM) operated at 80 keV. The particle core diameter was estimated by using ImageJ analysis of the TEM micrographs. UV–visible spectroscopic measurements were carried out with a UNICAM ATI UV4 spectrometer. The typical concentration of the particle solution was 0.27 μ M.

Electrochemistry. Electrochemical measurements were performed with a CHI 440 Electrochemical Workstation. A gold disk sealed in glass tubing was used as the working electrode, and a Ag/AgCl wire and a Pt coil were used as the (quasi) reference and counter electrode, respectively. Prior to use, the gold electrode was polished using 0.05 μ m alumina slurries followed by brief sonication in 0.1 M HNO₃, H₂SO₄, and Nanopure water, successively. The electrode was then subject to electrochemical etching by rapid potential sweeping (10 V/s) within the potential range of –0.2 to +1.2 V in 0.1 M H₂SO₄ until the characteristic voltammetric feature of a clean gold surface appeared. Prior to data collection, the electrolyte solution was deaerated by bubbling ultra-high-purity nitrogen for at least 10 min and blanketed with a nitrogen atmosphere during the entire experimental procedure.

AFM/STM Measurements. AFM and STM measurements were carried out with a Molecular Imaging PicoLE microscope. In an AFM study, the particles were dissolved in dichloromethane and drop-cast onto a freshly peeled mica surface

using a Hamilton microliter syringe. Typically, the samples were investigated at a scan rate of 1 Hz with 256 \times 256 pixel resolution during image capturing in tapping mode in air. In STM measurements, an atomically flat Au(111) substrate was used which was coated a priori with a decanethiol self-assembled monolayer to render the surface hydrophobic and to enhance the interactions with the DTC-capped particles. Again, the particles were deposited onto the substrate using the drop-cast method. A mechanically cut Pt/Ir tip was used in the STM measurements. *I*–*V* data were collected in the spectroscopy mode when the feedback loop was turned off. Initially, isolated nanoparticles were located by scanning in a large area (\sim 200 nm²), and stable, nondrifting images were then acquired by zooming into smaller areas. Two hundred *I*–*V* data points were collected in a typical voltage sweep of \pm 2 V. All *I*–*V* curves were averaged five times.

Results and Discussion

TEM Measurements. Transmission electron microscopy (TEM) has been used extensively to measure the nanoparticle core dimensions. Figure 1 shows the TEM micrographs for the three AgDTC particles along with their corresponding size histograms. First, it can be seen that the particles are all very well dispersed without any apparent aggregation. This indicates that DTC ligands bind very strongly onto the Ag surfaces and thus form a very efficient passivating layer onto the particle surface, as demonstrated previously with DTC-protected Au nanoparticles.²⁰ In addition, the average core diameter decreases with increasing initial ligand–metal feed ratio, e.g., from 4.84 \pm 2.15 nm for the (0.5 \times) sample to 3.03 \pm 1.17 nm (1 \times) and 2.49 \pm 0.79 nm (1.5 \times). Similar behaviors have also been observed in the synthesis of other nanoparticles with simple alkanethiols as the protecting ligands,²⁴ which could be understood as a result of more efficient passivation of the core surface at higher ligand concentrations during the growth (nucleation) of the particles.¹⁸ More interestingly, the size dispersity is modest and also exhibits a decrease with increasing ligand–metal feed ratio, e.g., 44.4% (0.5 \times), 38.6% (1 \times), and 31.7% (1.5 \times). For the (0.5 \times) particles, the histogram exhibits a bimodal distribution centered around 4 and 7 nm, respectively, whereas for the two smaller samples (1 \times and 1.5 \times), the majority of particles are below 4 nm.

Overall, these DTC-capped Ag nanoparticles are substantially smaller than those synthesized under similar conditions but with simple alkanethiols as the capping ligands, indicating that the DTC-based bidentate ligands provide better passivation on the particle growth and hence a smaller core size of the resulting Ag nanoparticles. It should be noted that, in most syntheses, silver nanoparticles with core diameter $<$ 3 nm are actually rather rare. For instance, Kang et al.¹⁶ synthesized Ag nanoparticles using dodecanethiols as the protecting ligands and found that the particle diameter was at around 7.7–7.9 nm whether the particles were synthesized in a two-phase or a one-phase route. The protocol presented above offers a very effective route toward the production of ultrasmall and stable Ag nanoparticles which may exhibit unique optical and electronic properties (vide infra).

UV–Vis Spectroscopy. It has been well-known that transition-metal nanoparticles typically exhibit a characteristic surface plasmon absorption band which superimposes onto the exponential decay Mie scattering profile, with the band intensity proportional to the particle size (volume).²⁵ In other words, a qualitative evaluation of the particle dimension can be obtained by simple UV–vis measurements. Figure 2 depicts the UV–

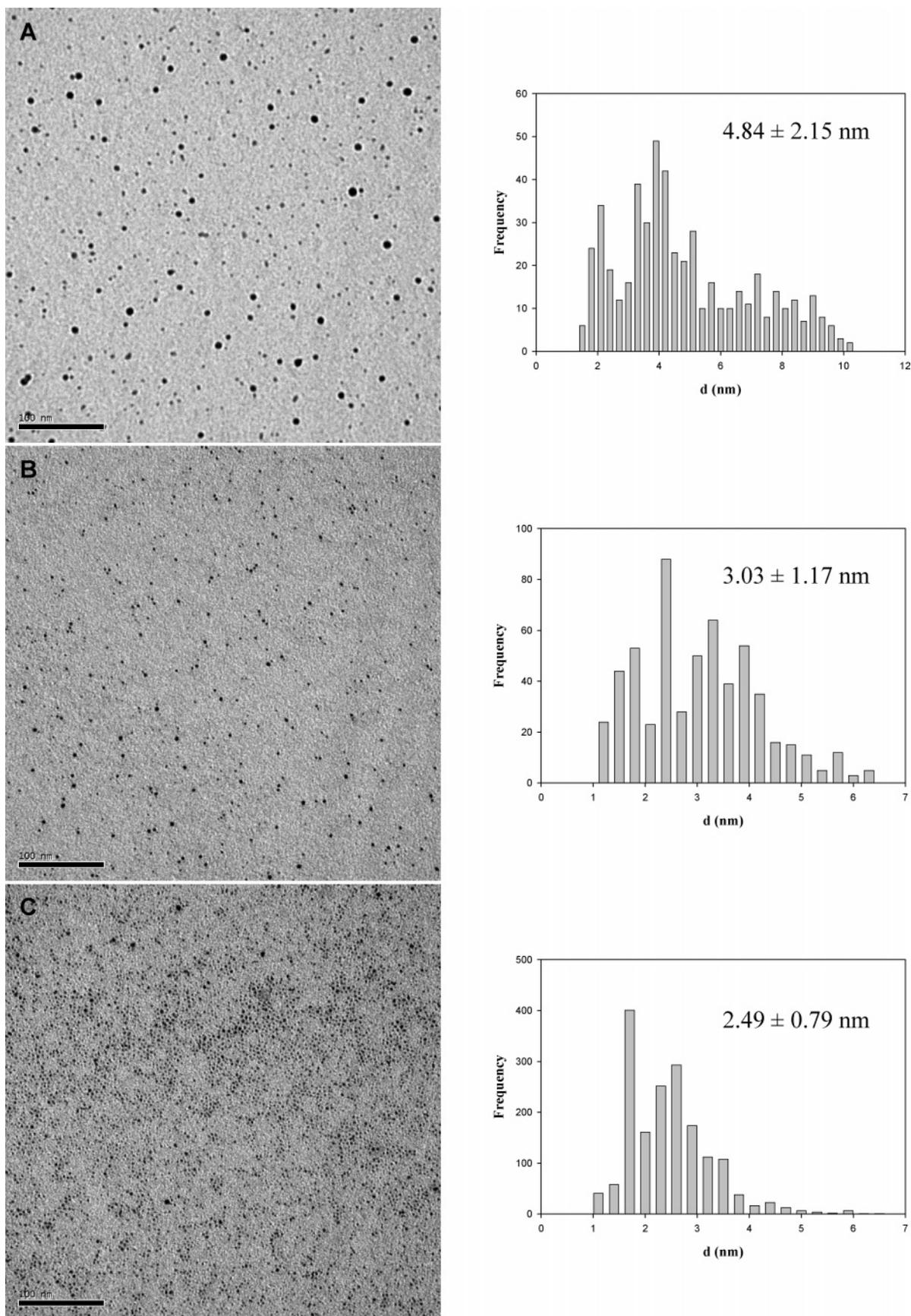


Figure 1. TEM micrographs of the AgDTC10 particles at varied initial ligand–metal feed ratios: (A) 0.5, (B) 1, and (C) 1.5. The corresponding core diameter histograms are shown to the right. The scale bars are all 100 nm.

vis absorption spectra of the three Ag particles synthesized above. It can be seen that for the (0.5 \times) sample, a very

pronounced peak at ca. 430 nm can be seen, which is characteristic of nanometer-sized Ag particles,²⁶ whereas for the

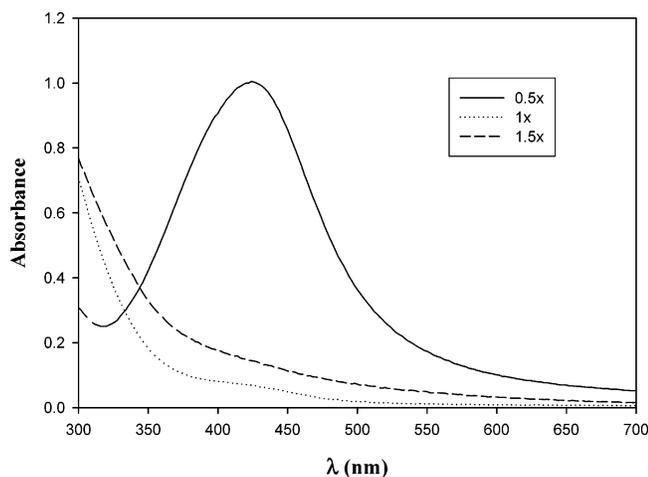


Figure 2. UV-vis absorption spectra of the three AgDTC10 nanoparticles at a concentration of ca. 1 mg/mL.

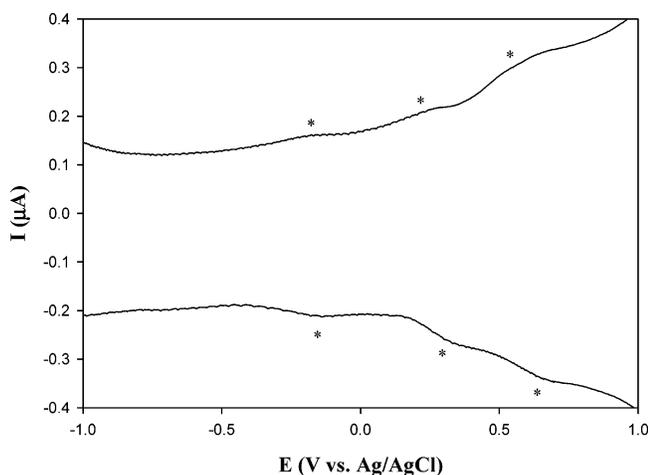


Figure 3. Differential pulse voltammograms of AgDTC10 (1.5 \times) nanoparticles at a gold electrode (area 0.1 mm²) in dichloromethane with 0.1 M tetrabutylammonium perchlorate (TBAP). Particle concentration 3.73 mg/mL. dc ramp 4 mV/s, pulse amplitude 50 mV, pulse width 200 ms. Asterisks mark the peak positions.

(1 \times) particles, the absorption peak at 430 nm is drastically weaker, and for the (1.5 \times) particles, the absorption profile is essentially featureless. These measurements are in agreement with the above TEM measurements (Figure 1), which show that the particle core dimension decreases significantly with the increase of the initial ligand-metal ratio. Similar behaviors have also been observed with gold nanoparticles,²⁴ where the surface plasmon resonance peak becomes broadened into the baseline with decreasing particle core size. With these ultrasmall particles, we anticipate observation of the quantized charging features in their electrochemical measurements, as detailed below.

Electrochemistry. The electrochemical responses for the smallest particles (1.5 \times) are shown in Figure 3, where differential pulse voltammetry (DPV) was carried out with the particles dissolved in dichloromethane with a 0.1 M tetrabutylammonium perchlorate (TBAP). It can be seen that, within the potential range of -1.0 to +1.0 V, there are at least three pairs of small but rather visible voltammetric peaks. (Similar features were also observed with the (1 \times) samples whereas only a featureless voltammetric profile was found with the (0.5 \times) sample, not shown.) These are ascribed to the quantized capacitance charging to the particle molecular capacitance, an analogy to the STM-based measurements of Coulomb staircase

involving individual particles (vide infra), akin to those with gold particles.⁵ From the potential spacing (0.40 V) between the neighboring charging peaks, we can estimate the respective particle molecular capacitance (C_{MPC}) as 0.40 aF. For comparison, the molecular capacitance for the (1 \times) particles is about 0.47 aF. In addition, the observed peak splitting (ΔE_p) is generally smaller than 50 mV, indicating kinetically (quasi)-reversible electron-transfer reactions.

For monolayer-protected nanoparticles, the molecular capacitance can be expressed as $C_{\text{MPC}} = 4\pi\epsilon\epsilon_0(r/d)(r + d)$.²⁷ By assuming the dielectric of the DTC monolayer to be 3 and the chain length of DTC to be 1.54 nm as calculated by Hyperchem, the average diameter for the particles that contribute to the quantized charging currents can be calculated to be about 1.78 nm (1 \times) and 1.58 nm (1.5 \times), respectively. These sizes are consistent with the virtually featureless responses in optical absorption measurements (Figure 2). Nonetheless, one may notice that these size values are somewhat smaller than those from TEM measurements (Figure 1). It should be noted that, in TEM measurements, the particle size is calculated by the statistical average of all the particles imaged in the micrograph, whereas in electrochemical measurements, only the fraction of particles with core diameter smaller than 3 nm will have a meaningful contribution to the quantized charging current (vide ante).²⁷

AFM and STM Studies. The particle dimensions were also evaluated by AFM measurements, where a drop of the particle solution was spread onto a freshly peeled mica surface and dried under a gentle nitrogen stream. The AFM micrographs exhibit very visible and well-dispersed nanosized particles. Because of tip convolution, particle core diameter was estimated by the heights in AFM measurements minus two DTC ligand chains (1.4 nm each). The AFM results (Supporting Information) for the three samples show the average core diameter of about 6.87 nm (0.5 \times), 2.89 nm (1 \times), and 2.08 nm (1.5 \times), respectively. While these values are close to those from the TEM measurements, there exists a clear discrepancy which may arise from the uncertainty of the molecular conformation of the DTC ligands when the particles are deposited onto the mica surface, as well as possible tip penetration into the particle-protecting layer during image acquisition.

STM measurements were also carried out with the (1.5 \times) particles. Figure 4 (top panel) shows a topological image of the particles spread onto a Au(111) surface that was coated a priori by an *n*-decanethiol self-assembled monolayer. Again, the dispersed arrangement of the particles strongly suggests the effective protection of the Ag particles by the DTC ligands, consistent with the TEM measurements (Figure 1). In addition, the corresponding $I-V$ profiles (blue lines) of two representative particles (labeled "A" and "B") are included in the subsequent panels, where the Coulomb staircase features can be clearly seen, and better resolved in the dI/dV plots (black curves in panels A and B). For instance, in panel A, several step increments of the current can be clearly seen within the bias range of -2.0 V to +2.0 V for particle "A" marked in the top panel (diameter \sim 1.6 nm), from which the particle capacitance can be estimated to be ca. 0.33 aF. With decreasing particle core size (panel B for particle "B" in the top panel, diameter \sim 0.8 nm), STM results show a featureless region of about 1.4 V centered around the zero potential position resembling the Coulomb blockade, beyond which the Coulomb staircase features start to emerge. This is ascribed to the emergence of a HOMO-LUMO energy gap for ultrasmall particles, as observed previously with the gold counterparts.^{5,28}

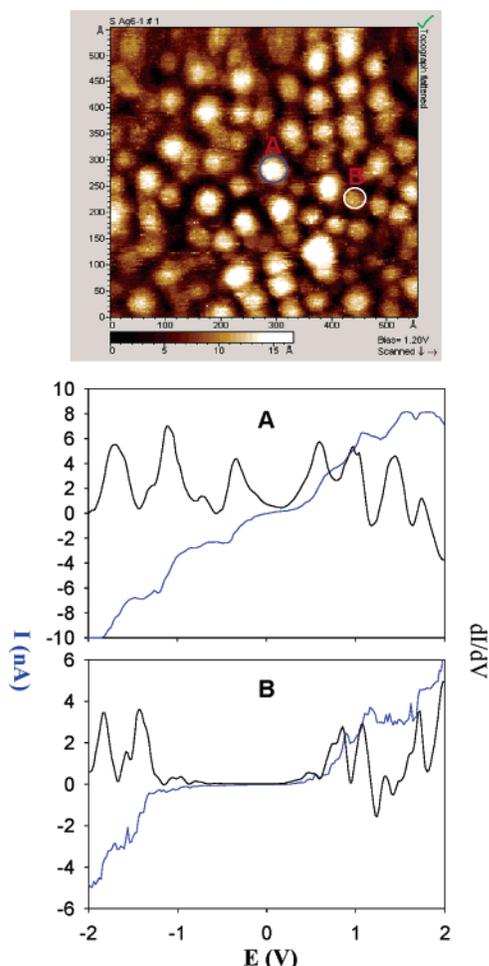


Figure 4. (top panel) STM topograph of AgDTC10 (1.5 \times) particles dispersed onto a decanethiol self-assembled monolayer that formed a priori onto a Au(111) surface. Middle and bottom panels exhibit the I – V (blue curves) and the corresponding dI/dV (black curves) profiles of two representative particles (labeled “A” and “B” in the top panel).

Summary

An effective protocol was established for the synthesis of silver nanoparticles with core diameter within the range of 2.5–5.0 nm by using dithiocarbamate derivatives as the protecting ligands. The particle core dimensions were found to be sensitively varied by the initial ligand–metal feed ratio, as attested by transmission electron microscopic measurements. When the feed ratio was >1 , the majority of the particles were found to be <4 nm in diameter, substantially smaller than that observed with the particles passivated by simple alkanethiols. The resulting particles exhibited interesting single-electron transfer characteristics both in STM measurements involving individual particles and in electrochemical quantized capacitance charging measurements.

Acknowledgment. The authors thank Prof. G.-Y. Liu (UC–Davis) and her students for their generous support in the

fabrication of Au(111) thin films. This work was supported in part by the NSF (CAREER Award CHE-0456130), ACS–PRF (39729-AC5M), and UC Energy Institute. M.C.T. is a UC LEADS Scholar.

Supporting Information Available: AFM topographs and particle core size histograms. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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