Surface Chemistry

Close-Packed Two-Dimensional Silver Nanoparticle Arrays: Quadrupolar and Dipolar Surface Plasmon Resonance Coupling


Abstract: Silver nanoparticles (NPs) ranging in size from 40 to 100 nm were prepared in high yield by using an improved seed-mediated method. The homogeneous Ag NPs were used as building blocks for 2D assembled Ag NP arrays by using an oil/water interface. A close-packed 2D array of Ag NPs was fabricated by using packing molecules (3-mercaptopropyltrimethoxysilane) to control the interparticle spacing. The homogeneous 2D Ag NP array exhibited a strong quadrupolar cooperative plasmon mode resonance and a dipolar red-shift relative to individual Ag NPs suspended in solution. A well-arranged 2D Ag NP array was embedded in polydimethylsiloxane film and, with biaxial stretching to control the interparticle distance, concomitant variations of the quadrupolar and dipolar couplings were observed. As the interparticle distance increased, the intensity of the quadrupolar cooperative plasmon mode resonance decreased and dipolar coupling completely disappeared. The local electric field of the 2D Ag NP array was calculated by using finite difference time domain simulation and qualitatively showed agreement with the experimental measurements.

Introduction

The optical properties of metal nanostructures have been of interest in materials chemistry owing to their unique color in the visible spectral range, known as surface plasmon resonance (SPR), which originates from the collective oscillations of free electrons on their surface. The resonance position can be tuned by controlling the structural components, shape, and size, as well as the refractive index of the surrounding dielectric medium.[1] Furthermore, the absorption peak can be shifted by the adsorption of biomolecules[2] or by coating the nanoparticle (NP) surface with other metal oxides,[3] which are often used for sensor or catalyst applications, respectively. Among various metals, such as gold, silver, copper, platinum, and palladium, that display SPR in the UV/Vis/near-IR region, silver exhibits the highest efficiency excitation,[4] and, compared with gold, a higher sensitivity to a change in the dielectric constant of the surrounding medium for biomolecule detection.[5] Moreover, through shape transformation, silver nanostructures were converted into hollow, porous, and frame nanostructures by using the galvanic replacement reaction with more noble metal ions, such as gold, palladium, and platinum, that have a higher redox potential than Ag+/Ag (0.80 eV versus a standard hydrogen electrode (SHE)).[6]

A large number of synthetic methods for the preparation of Ag NPs have been developed and improved for homogeneous size and shape controllability.[7] Wet chemical synthetic methods have been used to obtain high-quality NPs and for a better understanding of their formation mechanism. Chumanov and Evanoff synthesized sized-controlled (15–200 nm) Ag NPs based on the reduction of silver oxide by hydrogen gas, and they determined the dipole and quadrupole resonance modes of large Ag NPs.[8] Xia et al. synthesized silver nanocubes and cages by using the reduction of silver ions by ethylene glycol in the presence of poly(vinylpyrrolidone) (PVP).[9] Anisotropic silver structures, such as nanorods, nanowires, and nanobelts, have been synthesized by using the polyl process, plasmon excitation, and shape transformation through a thermal process, respectively.[10] Most of the synthetic methods for Ag NPs require a polyl process or high-temperature conditions.

A rational strategy for NP assembly and synthesis is an important issue in the utilization of NPs. Surfactant- or additive-based assembly of NPs are effective ways to achieve stable and large-scale films.[11] A strong near-field interaction between Ag NPs occurs when Ag NPs are assembled in a 2D array; this is termed the cooperative plasmon mode (CPM).[12] The quadrupolar character of the CPM is enhanced or quenched by controlling the particle size, interparticle distance, and surrounding dielectric medium.[13] As the interparticle distance increases, the sharp CPM resonance decreases and the extinction spec-
trum changes to noncoupling NPs. The assembly of Ag NPs with a nanogap distance shows additional enhanced optical properties for surface-enhanced Raman spectroscopy (SERS) applications.\[14\]

Herein, we report the optical properties of a 2D close-packed assembly of Ag NPs obtained with the assistance of 3-mercaptopropyltrimethoxysilane (MPTMS) as a spacer. We improved the seed-mediated synthetic method for the preparation of homogeneous Ag NPs without the need for a polyol at room temperature. The method exhibited good controllability over a broad range of NP sizes from 40 to 100 nm with a narrow size distribution and high yield. The dipolar and quadrupolar localized SPR modes were observed in the visible region. The Ag NPs with well-defined sizes and shapes were used as building blocks for 2D assembled arrays at the water/hexane interface. MPTMS in hexane played a key role in forming a close-packed Ag array without crystalline fusion between Ag NPs. On the other hand, a loose-packed 2D Ag array with large void areas and a longer interparticle distance formed when MPTMS was absent during formation of the 2D Ag array. Additionally, the morphology of Ag NPs was not maintained and they collapsed into irregular aggregates that caused crystalline fusion of Ag NPs at the water/hexane interface. In contrast, a regularly close-packed Ag array led to an intense quadrupolar CPM resonance and a dipolar red-shift relative to the solution of Ag NPs. Dipolar coupling and quadrupolar CPM resonance decreased as the interparticle distance of the Ag NP array increased.

**Results and Discussion**

It is noteworthy that the synthesis of relatively large Ag NPs (d > 50 nm) with a narrow size distribution is not an easy task compared with that for analogous Au NPs. The relatively easy oxidation of Ag NPs often complicates the reduction process of Ag ions, resulting in a broad size distribution of Ag NPs. We found that adding NaOH last, after the addition of the capping agent, Ag ions, Ag NP seeds, and mild reducing agent, to the growth solution dramatically increased the homogeneity of the resulting Ag NPs.\[15\] The addition of NaOH initiates the reduction of Ag ions onto the Ag NP seeds without creating new nucleation sites. By adapting this simple method, the size of the Ag NPs could be controlled up to about 150 nm with a narrow size distribution (the standard deviation was less than 10%).

Two-dimensional arrays of Ag NPs were prepared at a water/hexane interface by entrapping Ag NPs, as described in Figure 1. Figure 1 shows detailed step-by-step processes for Ag NP assembly at the water/hexane interface in the absence and presence of MPTMS in the hexane layer. The addition of ethanol decreases the dielectric constant of water (80 at 293 K) as a function of added total volume ratio, leading to destabil-
zation of Ag NPs in water, and consequently entrapment of NPs at the water/hexane interface. A photograph of entrapped Ag NPs reveals the characteristic metallic dull sheen due to optical coupling between the NPs (Figure 2E and J). The driving force for entrapment is the decrease in interfacial energy between water and hexane. The resulting 2D Ag NP array could be transferred to a silicon oxide substrate by horizontal lifting for FESEM analysis. Representative FESEM images are shown in Figure 2A–I for a variety of Ag NPs of different sizes (40–100 nm). In the absence of MPTMS, large void areas with a percentage area coverage of 23.6 to 26.2% (see the Supporting Information for details) were evident in all of the investigated Ag NPs (Figure 2A–D) because the residual surface charge density kept the NPs a certain distance apart. Furthermore, unstable Ag NP surfaces without a stabilizer can cause crystalline fusion between Ag NPs, as shown in the inset of Figure 2A–D. For NPs with an average size of 40 nm (Figure 2A), most of the NPs lost their original spherical shape and formed worm-like structures. Figure 2F–I shows FESEM images of the close-packed 2D arrays of Ag NPs that were prepared in the presence of MPTMS in the hexane layer, as described in Figure 1B. The calculated percentage area coverage of voids were drastically decreased to less than 9% (details are given in the Supporting Information). As reported by Pemberton et al., the thiol functional group in MPTMS can adsorb onto the Ag surface, resulting in the formation of a MPTMS self-assembled monolayer on the surface of Ag NPs. The adsorbed MPTMS forms a thin polymer coating on the Ag NPs through condensation and dehydration reactions. This thin polymer coating allows a close-packed 2D assembly of NPs at the interface without forming void areas between NPs. The close-packed 2D Ag NP array exhibits a strong mirror-like metallic sheen due to the strong optical coupling between NPs. The photographs in Figure 2E, J reveal the distinct difference in reflectivity of the resulting 2D arrays of NPs without and with MPTMS, respectively. The adsorption of organic molecules on the surface of NPs decreases their surface charge and enhances van der Waals interactions that lead to close-packing of the NPs. Furthermore, the polymerized layer of MPTMS on the surface of the NPs serves as a stabilizer by preventing aggregation and crystalline fusion, while maintaining the spherical shape, as shown in the insets of Figure 2F–I. Compared with the upper panels (prepared in the absence of MPTMS), NPs in the lower panels (prepared in the presence of MPTMS) show clear boundaries without fusion or shape transformation. It is noteworthy that the clear boundary of individual NPs is important in terms of investigating the cooperative surface plasmon coupling of NPs in close proximity (see below).

Figure 3 shows the UV/Vis/near-IR extinction spectra of Ag NPs with sizes ranging from 40 to 100 nm that correspond to the samples in the FESEM images of Figure 2. Line a in each panel of Figure 3 shows the extinction spectrum of Ag NPs dispersed in water. The observed peak maximum of the dipole surface plasmon mode systematically red-shifted from 420 to 441, 475, and 515 nm, as the size of the NPs corresponding to (39 ± 3), (59 ± 5), (79 ± 6), and (102 ± 8) nm, respectively, increased. The extinction modes were fairly narrow and represented the monodispersive characteristics of the Ag NPs; this is in good agreement with FESEM analysis. As the size of the NPs increased to 79 nm (Figure 3C), an additional peak appeared at 405 nm that was assigned to a quadrupole mode induced by phase retardation of the surface electron oscillation. The peak at 415 nm became more distinct as the size of the NPs became larger (ca. 102 nm), and the dipole mode became broader relative to that of smaller NPs. Line b in Figure 3 represents the UV/Vis/near-IR extinction spectrum of the 2D assembly of Ag NPs on a glass substrate prepared in the absence of MPTMS by following the scheme in Figure 1A. Regardless of the NP size, all of the investigated samples showed a very broad extinction profile from 400 to 1200 nm without noticea-
ble features; this is similar to the optical spectrum for a thin Ag film on a glass substrate. This monotonic extinction profile is attributed to the continuous contact of Ag NPs without distinct boundaries, as evident in the FESEM analysis (Figure 2A–D). Of central interest here is the UV/Vis/near-IR extinction spectra of close-packed Ag NPs prepared in the presence of MPTMS. Line c in Figure 3 indicates different extinction profiles as a function of NP size. When the NP size was small (Figure 3A,B), one distinct feature in the UV/Vis/near-IR spectra was the observation of quadrupolar coupling at 414 and 389 nm from the 2D Ag NP array, respectively, compared with solution-phase NPs. Given that there is no quadrupole mode in the solution phase (Figure 3A,B), it is interesting to observe the quadrupole modes that result from coherent electron oscillations in adjacent particles in the close-packed 2D Ag NP arrays. In the previous theoretical consideration, it was reported that a minimum NP size of 30 nm and a minimum array size of 50 particles were required to produce enough coupling of quadrupole modes to give narrow lines. Although our samples met the theoretical requirements for coupling of quadrupole modes to give narrow lines, it was found that coupling of dipole modes was quite strong and appeared at 691 and 723 nm for d = 40 and 60 nm, respectively (Figure 3A,B). The regular arrangement of close-packed Ag NPs without crystalline fusion contributes to the efficient coupling of dipole modes. For sizes larger than about 80 nm, the dipole mode (at 737 nm) and the quadrupole mode (at 376 nm) became strong, sharp features at shorter wavelengths. The quadrupole mode became even stronger with a very sharp peak at 380 nm for NPs larger than 100 nm (Figure 3D). The homogeneous close-packed and well-defined spherical shape of Ag NPs in the 2D array allowed the quadrupolar intensive CPM resonance and dipolar coupling. The position of the broader peak (dipole mode) of the dried 2D Ag array was red-shifted relative to the peak from Ag NPs in aqueous solution and is accounted for by dipolar coupling between neighboring Ag NPs.

To analyze the cooperative coupling of surface plasmon modes in detail, we plotted the observed intensity of dipolar and quadrupolar SPR modes (Figure 4A) and peak position (Figure 4B) of the close-packed 2D Ag array as a function of NP size. It is known that the excitation of SPRs induces oscillation of the local field surrounding Ag NPs. When the NPs are closely positioned, the local field from each NP overlaps, and consequently, the near-field interaction occurs. In a previous report, for Ag NPs that are relatively far apart in 2D arrays, Chumanov and Malynych observed only a strong coupling of the quadrupole mode, whereas the dipole mode was significantly dampened. They attributed this dampening of the dipole mode to symmetrically forbidden coupling of dipole modes in the 2D array, and reported that the dipole mode from each NP could not interact with all neighboring NPs in the same manner. However, quadrupole coupling meets the requirement for the same type of interaction and survives under the given conditions. In contrast, strong coupling of dipole modes, in addition to the coupling of quadrupole modes was observed when the interparticle distance was very short and each NP was separated by only a thin layer of polymer. Under these conditions, it is expected that the local field from each NP would overlap to a maximum extent, and coupling would extend beyond the closest neighbor NPs, that is, the CPM will become very significant due to short interparticle separation. Close proximity between Ag NPs induces the effective coupling of surface plasmon modes of individual NPs, including dipole and quadrupole modes. The extinction intensity of quadrupolar CPM increased as the size of the Ag NPs increased (Figure 4A). Zou et al. reported similar findings for NPs in 2D arrays based on theoretical calculations. The coupling sensitivity for the quadrupole mode was 0.02 Ext. per nm, which was higher than the 0.005 Ext./nm for the dipole mode as

![Figure 3](image-url) UV/Vis/near-IR spectra for different sizes of Ag NPs suspended in water (a) and on a glass substrate with loose- (b) and close-packed (c) 2D array. Size of the NPs: A) 30, B) 50, C) 70, and D) 102 nm.

![Figure 4](image-url) Graphs of SPR A) intensity and B) peak position versus the size of the Ag NPs. In each spectral window, the traces indicate dipole (■) and quadrupole (▲) modes.
a function of NP size. The observed difference in coupling sensitivity reveals that quadrupolar coupling becomes more significant than dipole coupling as the NP size becomes larger. The larger the NPs size, the more the collective oscillation of surface free electrons will be phase-retarded relative to dipole oscillation. This feature is evident for Ag NPs suspended in the aqueous phase (a in Figure 3A–D). Another noticeable difference between the dipole and quadrupole couplings is the peak shift direction. Figure 4B shows the red-shift of dipolar coupling from 691 to 758 nm as the particle size increased from 39 to 102 nm. In contrast, the quadrupole mode shifted from 414 to 380 nm as the size of the NPs increased.

To further investigate the dependence of surface plasmon coupling on the interparticle distance, a well-arranged 2D Ag NP array with MPTMS at the water/hexane interface was embedded in a elastomeric polydimethylsiloxane (PDMS) film with dimensions of 1×1 cm. The Ag NP decorated PDMS film was biaxially stretched from 1 to 3 mm, as shown in Figure 5A.

Representative FESEM images show increasing interparticle distance of the 2D Ag NP array before and after biaxial stretching (Figure 5B and C, respectively). After stretching, the interparticle distance increased from (5 ± 2) to (32 ± 17) nm. The corresponding UV/Vis/near-IR spectra exhibit significant differences in surface plasmon coupling dependency on interparticle distance. The unstretched film initially showed two modes at 424 and 751 nm for quadrupole and dipole coupling, respectively. As the film was systematically stretched from 1 to 2 and 3 mm biaxially, the dipole mode suddenly became very weak and disappeared after stretching beyond a certain range (ca. 2 mm), whereas the quadrupolar CPM resonance was retained. Although the intensity of the quadrupole mode coupling became weaker as the film was stretched, the peak survived until the dipole mode disappeared. Surprisingly, this observation clearly indicates that the dipole coupling has shorter distance characteristics than the quadrupole mode coupling in the near-field character of the coupling. It is expected that, as the film is stretched further, the quadrupole mode coupling would gradually weaken and surface plasmon features of individual NPs would appear. However, our film could not be stretched further due to insufficient elasticity of the PDMS film. It is noteworthy that our NP arrays have much higher NP density and a shorter interparticle distance than those reported previously. Chumanov et al. ascribed the dominant appearance of quadrupole coupling to the symmetry-forbidden nature of dipole coupling and symmetry-allowed quadrupole characteristics. Surprisingly, in our case, the short interparticle distance separated only by MPTMS molecules allows dipolar coupling in addition to quadrupolar coupling.

Figure 6 illustrates the calculated $|E|^2$ distribution maps before and after biaxial stretching of the 2D Ag NP (diameter: 100 nm) arrays obtained through finite difference time domain (FDTD) simulation. Hexagonal packing was used to show the field behavior between Ag NPs at the peak positions of quadrupole and dipole coupling modes (424 and 751 nm, respectively). The high local field was calculated based on hexagonal close-packed 2D Ag NP arrays (Figure 6A and C) having a short gap distance (5 nm) before stretching. On the other hand, the intensity of the local electric filed decreased after biaxial stretching of the 2D Ag NP arrays (Figure 6B, D, gap distance: 32 nm). Of essential interest here is a comparison of the quantity of decreased local electric field (quadrupole and dipole...
modes) when different wavelengths of laser irradiation (424 and 751 nm) are used for quadrupole and dipole excitation. When the 424 nm laser (peak position of quadrupole coupling mode) was used for the simulation, the maximum intensity of local electric field decreased from 4.7 to 4.0 (18%) after biaxial stretching. However, a dramatic decrease in the local electric field from 11.1 to 5.2 (53%) was observed from irradiation with the 751 nm laser. From the calculation results, qualitatively we can conclude that the quadrupole mode coupling survives longer distances than the dipole mode coupling, which supports the experimental UV/Vis absorption results. The method to fabricate a close-packed 2D array and control the gap distance could be further applied to other shapes of NPs, such as gold nanorods (Supporting Information, Figure S3). A strong dipolar coupling could also be observed due to the high-quality close-packed condition and followed the same trend as the gap distance increased, but the quadrupolar mode could not be observed because the dimension condition of the utilized nanorod did not satisfy retardation of the surface plasmon.

Near-field optical coupling between NPs is often utilized to enhance the Raman signal of adsorbates. In general, it is known that the nanoscale interparticle distance of NPs induces strong Raman enhancement due to their coupled electromagnetic field at the junctions.\[24\] Because a well-arranged Ag NP 2D array contains many such hotspots for the enhanced local field through surface plasmon coupling, the 2D Ag array can be used as an effective SERS substrate to maximize Raman signals.\[24\] Figure 7 shows SERS spectra and the corresponding confocal Raman mapping images of mercaptobenzene utilized as an adsorbate on 2D Ag NP arrays prepared with and without MPTMS. A comprehensive peak assignment of the spectral features has been reported and is not described herein.\[25\] As clearly evident in the SERS spectra, the gray trace in Figure 7 A (close-packed array prepared in the presence of MPTMS) shows signals that are about twice as strong as those of the black trace (loose-packed array prepared in the absence of MPTMS). Although the close-packed 2D Ag array (gray trace in Figure 7 A) contains a thin MPTMS coating layer that positions the adsorbate further from the Ag NP surface compared with the relatively clean 2D array (black trace), the electromagnetic field exerted on the adsorbate is stronger with the more densely packed array. As clearly shown in the FESEM analysis, we believe that the well-defined NP boundaries contribute to the effective enhancement of local field coupling of Ag NPs in the 2D array. Significantly, the corresponding confocal Raman image of the close-packed 2D Ag NP array exhibited strong and homogeneous Raman signals over the entire substrate, which was in sharp contrast to the case of the loose-packed 2D Ag NP array (Figure 7 B and C, respectively). This observation is in good agreement with FESEM analysis, which shows the homogeneous close-packed film morphology of Ag NPs with clear individual boundaries.

Conclusion

We prepared Ag NPs with a broad range of sizes from 40 to 100 nm in high yield by using an improved seed-mediated method. The homogeneous Ag NPs were used as building blocks for close-packed 2D Ag NP arrays by using a water/hexane interface. The close-packed 2D Ag NP array was fabricated by using MPTMS as a spacer that contributed to the preservation of the boundaries of individual NPs. Without MPTMS, the Ag NPs were unstable, which resulted in crystalline fusion at the water/hexane interface. Close packing allowed effective local near-field interactions, which resulted in the appearance of strong couplings in the dipole and quadrupole modes. As the NP size became larger, stronger quadrupole mode coupling was observed relative to that of dipole mode coupling. Additionally, as the interparticle distance became larger, the dipole mode coupling disappeared, whereas the quadrupole mode coupling survived until the interparticle distance was about 32 nm; this indicated that the quadrupole mode coupling had longer distance coupling characteristics than those of the dipole mode coupling. The local electric field of the 2D Ag NP array was calculated by using FDTD simulation and showed good agreement with the experimental measurements. This new strategy for the fabrication of close-packed NP arrays introduces a new pathway for the development of highly sensitive sensors and optical filters and/or related optoelectronic devices. Finally, the close-packed Ag NP arrays showed stronger SERS than that of loose-packed Ag NP arrays due to their well-defined NP boundaries, which enhanced the local field coupling to a maximum extent.

Experimental Section

Synthesis of Ag nanospheres

Ag seeds were prepared by reducing AgNO\(_3\) with NaBH\(_4\). In detail, a 10 mM solution of NaBH\(_4\) (600 \(\mu\)L) cooled at 4 °C in a refrigerator for 15 min was mixed with a 0.25 mM solution of AgNO\(_3\) (2 mL)
and a 100 mM solution of cetyltrimethylammonium bromide (CTAB; 18 mL) in a 20 mL glass bottle. After stirring for 2 min, the mixture was kept for about 2 h at room temperature until the color of the solution had turned from colorless to light yellow. Ag NPs were prepared by mixing a 0.1 M solution of CTAB (200 mM), a 0.01 M aqueous solution of AgNO₃ (5 mL), a 0.1 M aqueous solution of ascorbic acid (10 mL), a 0.1 M aqueous solution of NaOH (2 mL), and the desired amount of Ag seed solution, and allowing the mixture to react for about 4 h at room temperature without stirring. The size of the Ag NPs was controlled by varying the volume of the Ag seed solution; 0.9 mL, 0.1 mL, 40 μL, and 20 μL of Ag seed solutions were used to grow Ag NPs of approximately 40, 60, 80, and 100 nm, respectively. The products were collected by centrifugation at 6000 rpm for 25 min, 5000 rpm for 20 min, 4000 rpm for 20 min, and 4000 rpm for 20 min (corresponding to the above solutions). After centrifugation, the supernatant was replaced with distilled water.

Preparation of the 2D Ag array
NP solution (10 mL) was transferred into a homemade Teflon trough, and hexane (2 mL) was added to the solution to form a hexane/water interface. A 1 × 10⁻⁶ M solution of MPTMS (1 mL) was added to the top hexane layer and ethanol (ca. 5 mL) was added dropwise at a rate of 30 mL/h⁻¹ with a mechanical syringe pump (KDS101). Ethanol played the role of transporting NPs from the aqueous solution to the hexane/water interface region. Hexane was then evaporated to allow the linkage of MPTMS. Then, a mixture of vinyl-terminated PDMS (0.5 mL), curing agent (0.5 mL), and hexane (1 mL) was added to the top layer of the Ag NP array and dried in the oven for 2 h (at 70 °C). The 2D Ag NP array collected on silicon wafers was used for FESEM and energy-dispersive X-ray spectroscopy (EDS) measurements.

FDTD simulation
A MEEP program (version 0.20.3), developed by Johnson et al.[26] was used. Along the light propagating z axis, 300 nm thick perfect matching layers (PML) were placed at both ends. Free spaces (1.0 μm thick) were placed below the top PML and above the bottom PML. Between these two free spaces, the 2D array Ag NPs was placed. An electromagnetic light source was set on 30 nm below the top PML, which was propagated as a plane-wave along the z axis. A periodic boundary condition was applied to all x, y, and z axes, so that the target structure was a repeating unit of an infinitely large 2D film. A contact spacing of 5 nm was placed between any neighboring spheres for the close-packed condition, whereas 32 nm spacing was used for the biaxial stretching condition. The spheres at the x or y boundaries were arranged to satisfy the periodic boundary conditions. For the dispersion equation of optical constants of Ag, the complex dielectric constant data of Johnson and Christy[25] were used to fit Equation (1), based on an extended Durie model.[28]

\[
\varepsilon(\omega) = \varepsilon_\infty + \frac{A}{\omega_0^2 + i\omega_0^2} + \frac{B\omega_0^2}{\omega_0^2 - \omega_0^2 + i\omega_0^2}
\]  

(1)

With fitting parameters similar to those reported in the literature,[25] an excellent fit of \(\varepsilon(\omega)\) to Johnson and Christy’s data was made in the wavelength range between 500 and 2000 nm. A subpixel smoothing[26] was used for the dielectric constants of the Ag and free cells. A computational memory over 45 GB, a parallel computer system (32 nodes, 2 CPUs and 2 GB in each node) was employed.

Acknowledgements
This work was supported by the National Research Foundation of Korea (National Leading Research Lab: 2011-0027911) and the Human Resources Development program (no. 20124010203270) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea Government Ministry of Trade, Industry and Energy.

Keywords: nanoparticles · optical properties · silver · surface chemistry · surface plasmon resonance

Received: December 12, 2014
Published online on March 4, 2015