

# Controlled Growth of Layered Silver Stearate on 2D and 3D Surfaces

Seung Joon Lee, Sang Woo Han, and Kwan Kim

**This investigation confirms that silver stearate consists of an infinite-sheet, two-dimensional, nonmolecular layered structure. Scanning electron microscopy, X-ray diffraction, and infrared spectroscopy reveal the following: plate-like morphology is identified from the SEM image, XRD peaks can be indexed to the (0k0) reflections of a layered structure, and infrared peaks show that alkyl chains are present in an all-trans conformational state with little or no significant gauche population. Based on these structural characteristics, we demonstrate that silver stearate, a prototype of layered organic-inorganic hybrid material, can be grown not only in a designed two-dimensional pattern but also in three-dimensionally ordered ways by using carboxyl-group terminated nanoparticles as a template.**

**Keywords:** Silver stearate, nanoparticle, layered structure.

## I. Introduction

In the past decade, the number of organic-inorganic hybrid materials that exhibit alternating two-dimensional (2D) molecular assemblies of organic and inorganic constituents has expanded considerably, encompassing a host of technologically relevant materials. Specific material properties, e.g., stiffness, strength, weight, nonlinear optical behavior, electrical conductivity, photochemical charge transfer, and ferromagnetism, can be manipulated by systematic variations in the structure and properties of the organic and inorganic constituents at the molecular level [1].

Silver alkane carboxylate ( $\text{AgCO}_2\text{R}$ ) is one class of organic-inorganic hetero-structured materials that show a well-developed progression of intense X-ray reflections; these intense X-ray reflections are associated with the three-dimensionally stacked silver carboxylate layers [2], [3]. Due to the specific arrangement of Ag atoms in a layer,  $\text{AgCO}_2\text{R}$  possesses 2D conductivity in a solid state [4].  $\text{AgCO}_2\text{R}$  also decomposes into alkane carboxylate-derivatized silver nanoparticles [5], [6]. To develop technologically relevant organic-inorganic hybrid materials, detailed structural information is needed for a series of layered compounds. For successful application of these materials, it is also desirable to assemble organic-inorganic hybrid materials in two-dimensionally ordered ways on a solid substrate. To achieve this aim, we demonstrate that a prototype  $\text{AgCO}_2\text{R}$ , silver stearate, can be grown site-selectively on a solid substrate onto which organic monolayers have previously been assembled in a designed pattern. We also demonstrate that  $\text{AgCO}_2\text{R}$  can be grown even in three-dimensionally ordered ways by using carboxyl-group terminated nanoparticles for a template.

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## II. Characteristics of Silver Stearate in Bulk

We used a two-phase method to prepare the silver stearate [6]. Briefly, a 0.05 M aqueous solution of  $\text{AgNO}_3$  (99+%, Aldrich) was added dropwise to an equimolar stearic acid (99+%, Aldrich) solution in toluene. After three hours of vigorous stirring, we filtered the resulting white precipitate, washed it consecutively with ethanol, toluene, and cold water, and dried it in a vacuum. Reference [6] previously reported the detailed structural characteristics and thermal behavior of silver stearate [6]. A scanning electron microscopy (SEM) image of the as-prepared silver stearate showed a typical layered morphology (Fig. 1(a)); the image was obtained with a JSM 840-A scanning electron microscope at 20 kV. The X-ray diffraction (XRD) data (Fig. 1(b)) also reflected three-dimensionally stacked silver carboxylate layers with a large interlayer lattice dimension; the XRD pattern was obtained on a Philips X'PERT MPD diffractometer at an angular resolution of  $0.05^\circ$  using  $\text{Cu K}\alpha$  ( $1.5419 \text{ \AA}$ ) radiation. All the intense reflections in Fig. 1(b) can be indexed as  $(0k0)$ . Each layer of silver carboxylate, however, is separated from the neighboring layer by twice the length of the alkyl chain. The inset of Fig. 1(b) also lists the interlayer spacings derived on these grounds from different reflections. The averaged interlayer spacing is  $48.36 \pm 0.22 \text{ \AA}$ .

## III. Controlled Growth of Silver Stearate on 2D- and 3D-Surfaces

### 1. Silver Stearate Grown on 2D Patterned Organic Monolayers

Figure 2 schematically describes the experimental procedure for the patterned growth of the layered silver stearates on carboxylic-group terminated organic monolayers. We prepared gold substrates by resistive evaporation of titanium (5 nm) and gold (100 nm) on precleaned glass slides. Microcontact printing ( $\mu\text{CP}$ ) for the fabrication of patterned monolayers on Au was performed following the published procedure [7]. Briefly, an aliquot of 10 mM ethanolic solution of 16-mercaptohexadecanoic acid (16-MHDA) was spin-coated on a poly(dimethylsiloxane) (PDMS) stamp at 3000 rpm for 30 seconds, and the stamp was brought into contact with the Au substrate for 10 seconds. Subsequently, the Au substrate was washed with a 1 mM ethanolic solution of benzenethiol for the passivation of the unprinted regions. We immersed the resulting patterned substrate in a mixture of an aqueous  $\text{AgNO}_3$  solution (2 mM) and a toluene solution of stearic acid (2 mM). After stirring the solution for two hours, we thoroughly washed the substrate with water, toluene, and ethanol, and then dried

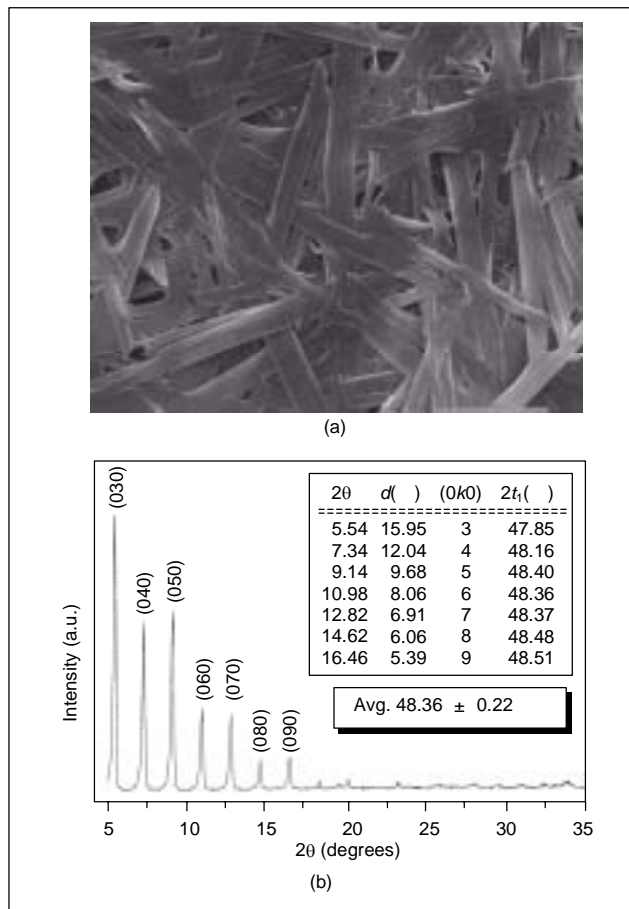


Fig. 1. (a) SEM image of powdered silver stearate and (b) XRD pattern of silver stearate; the interlayer spacings derived from different reflections are listed in the inset.

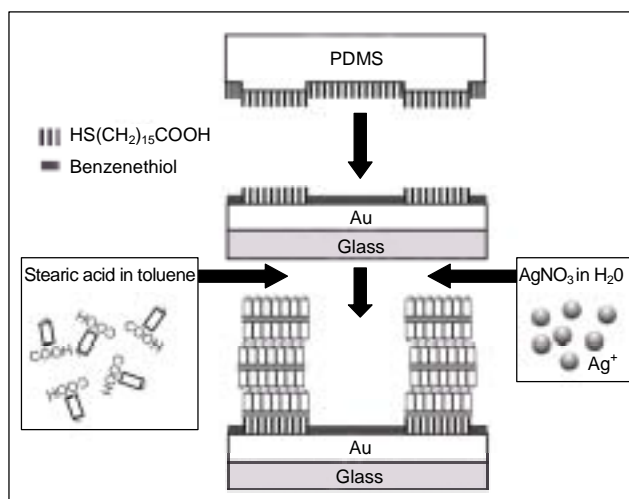


Fig. 2. Flowchart showing the strategy for growing 2D patterned silver stearate. PDMS: poly (dimethylsiloxane).

it under a stream of nitrogen. Using XRD, atomic force microscopy (AFM), and IR spectroscopy, we obtained evidence of the patterned growth of the silver stearate on gold

in a layered structure; a Digital Instruments Nanoscope IIIa scanning probe microscope obtained the AFM image, and a Bruker IFS 113v FT-IR spectrometer captured the IR spectrum. Figure 3(a) shows the XRD pattern for silver stearate grown on Au. The average interlayer spacing is  $48.96 \pm 0.54 \text{ \AA}$ , which is in agreement with the interlayer spacing of bulk silver stearate (Fig. 1(b)). A typical AFM image (Fig. 3(b)) shows that layered silver stearates are formed exclusively on the hydrophilic region of the patterned monolayers. The height difference between the reacted and the unreacted regions is about  $150 \text{ \AA}$ , corresponding to the formation of more or less three layers of silver stearate on gold. A molecular resolution image (Fig. 3(c)) indicates further that the silver stearate grown on gold assumes triclinic subcell packing. The patterned silver stearate shows hydrophobic behavior to water droplets, which implies the outermost surface is composed of methyl groups. The inset in Fig. 3(c) reveals that the nearest distances between the lattice points are about  $4.3$  and  $4.8 \text{ \AA}$  ( $x \times y$ ). These values are in good agreement with the triclinic unit cell parameters Tolochko et al. measured using Ag K-EXAFS [3].

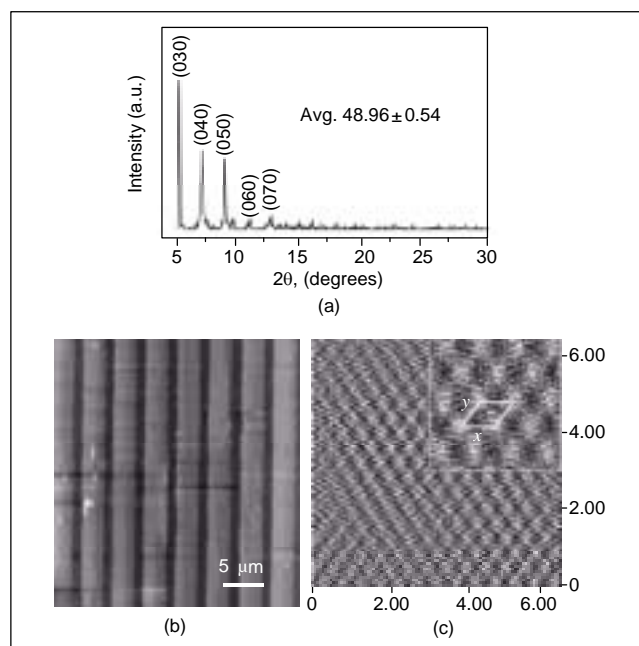


Fig. 3. (a) XRD pattern, (b) AFM image of the patterned silver stearate on Au, and (c) enlarged molecular resolution AFM image of the area where silver stearates are formed ( $x$ :  $4.3 \text{ \AA}$ ,  $y$ :  $4.8 \text{ \AA}$ ).

Figure 4(a) shows the IR spectrum of the silver stearate formed on the patterned substrate. Characteristic IR bands of stearate are observed not only in the high frequency region ( $2954$ ,  $2916$ ,  $2871$ , and  $2848 \text{ cm}^{-1}$ ) but also in the low frequency region ( $1517$ ,  $1470$ ,  $1419$  and  $717 \text{ cm}^{-1}$ ). We assign two strong peaks at  $2848$  and  $2916 \text{ cm}^{-1}$  to the symmetric

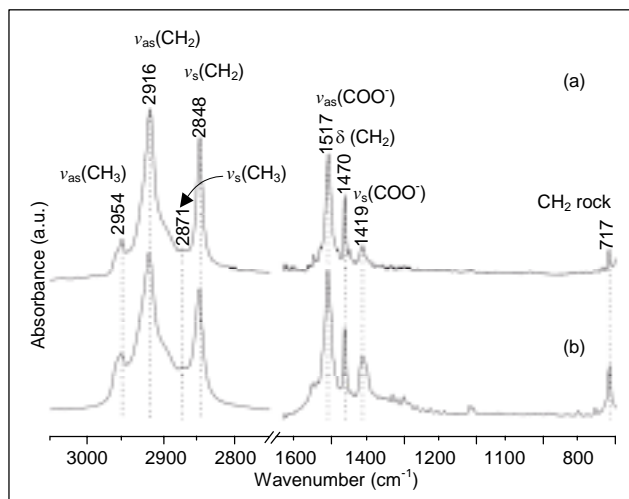


Fig. 4. IR spectra of silver stearate: (a) synthesized by a two-phase (water/toluene) method and (b) grown on Au. The spectrum (a) was measured in diffuse reflectance mode while the spectrum (b) was obtained in external reflection mode.

( $\nu_s(\text{CH}_2)$ ) and the antisymmetric ( $\nu_{as}(\text{CH}_2)$ ) stretching vibrations of the methylene groups, respectively. These modes usually lie in narrow ranges of  $2846$ – $2850$  and  $2915$ – $2918 \text{ cm}^{-1}$ , respectively, for all-trans extended chains [10], and in the distinctly different ranges of  $2854$ – $2856$  and  $2924$ – $2928 \text{ cm}^{-1}$  for disordered chains [11]; the alkyl chains in silver stearate should thus be fully extended. The scissoring and rocking modes of the methylene group observed at  $1470$  and  $717 \text{ cm}^{-1}$ , respectively, clearly suggest that silver stearate consists of triclinic packing with two chains per unit cell [12], which is in agreement with the AFM measurement. Other bands at  $2954$ ,  $2871$ ,  $1517$ , and  $1419 \text{ cm}^{-1}$  can be attributed to the  $\nu_{as}(\text{CH}_3)$ ,  $\nu_s(\text{CH}_3)$ ,  $\nu_{as}(\text{COO}^-)$ , and  $\nu_s(\text{COO}^-)$  modes of silver stearate, respectively [13]. All of the observed IR bands for patterned silver stearate are thus exactly the same as those of layered silver stearate prepared in solution by a two-phase method [6] (see Fig. 4(b)). Hence, we surmise that the silver stearate is actually grown on a patterned substrate with a single-crystalline feature rather than with a polycrystalline one.

A plausible mechanism of the site-selective growth of silver stearate on a hydrophilic monolayer is that at the initial stage,  $\text{Ag}^+$  ions bind to terminal carboxyl groups of 16-MHDA, and then stearic acids bind to these  $\text{Ag}^+$  ions to form a stable Ag-COO slab. Additional stearic acids anchor on the methyl-terminated region to form a lipid-like bilayer by hydrophobic interaction; the alkyl chains interpenetrate to a fair extent in the bilayer [6]. Subsequently, new  $\text{Ag}^+$  ions are bonded to the terminal carboxyl groups of the bilayer, and then new stearic acids assemble on these  $\text{Ag}^+$  ions to form another Ag-COO slab and lipid-like bilayer. Continuation of these processes can result in multilayered silver stearate on patterned Au.

## 2. Silver Stearate Grown on 4MBA-Capped Au Nanoparticles

To model 3D surfaces, we prepared 4-mercaptobenzoic acid (4-MBA, 99+%, Aldrich)-capped Au nanoparticles through a place exchange reaction [8] of pentanethiol (PT)-capped Au nanoparticles [9] and 4-MBA so that the outermost regions of the nanoparticles were composed of carboxyl groups. Briefly, the PT-capped Au nanoparticles and 4-MBA (1 mM) were codissolved in tetrahydrofuran (THF, 30 mL) under constant stirring for a week. We then removed the solvent using a rotary evaporator and washed the remaining sample thoroughly with diethyl ether to remove excess 4-MBA. According to the transmission electron microscope (JEM-200CX, 160 kV) image, the core sizes of the 4-MBA-capped Au nanoparticles were uniform with an average diameter of  $4.0 \pm 1.5$  nm, and the UV/vis spectrum in ethanol showed a characteristic surface plasmon absorption band of Au nanoparticles at 525 nm. Infrared spectroscopy revealed that the surfaces of the nanoparticles were terminated with carboxyl groups; see, for instance, the characteristic carbonyl stretching ( $\nu(\text{C}=\text{O})$ ) band at about  $1700 \text{ cm}^{-1}$  in Fig. 7(b).

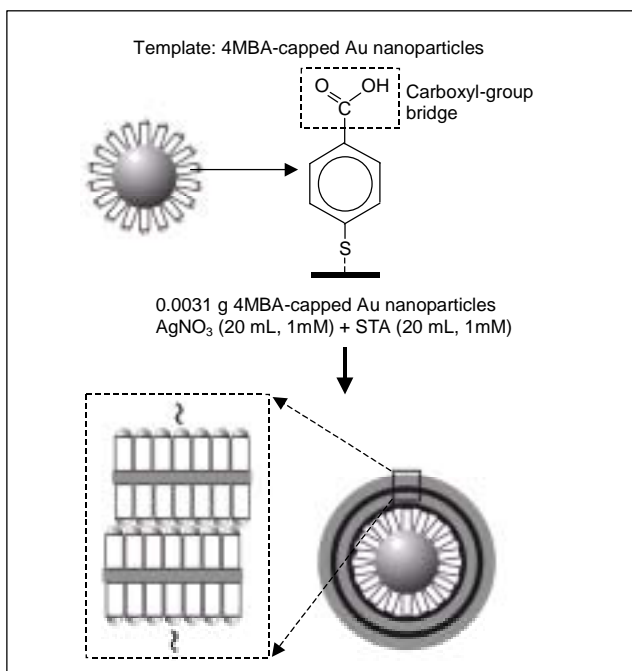


Fig. 5. Flowchart showing the strategy for growing silver stearate on Au nanoparticles.

Figure 5 schematically describes the growth of layered silver stearates on carboxyl-group terminated Au nanoparticles. To execute the experiment, we initially injected 0.0031 g of 4-MBA-capped Au nanoparticles in methanol (1 mL) into 20 mL of AgNO<sub>3</sub> in methanol (1 mM). After 10 min, we added 20 mL solution of stearic acid in methanol (1 mM) dropwise into

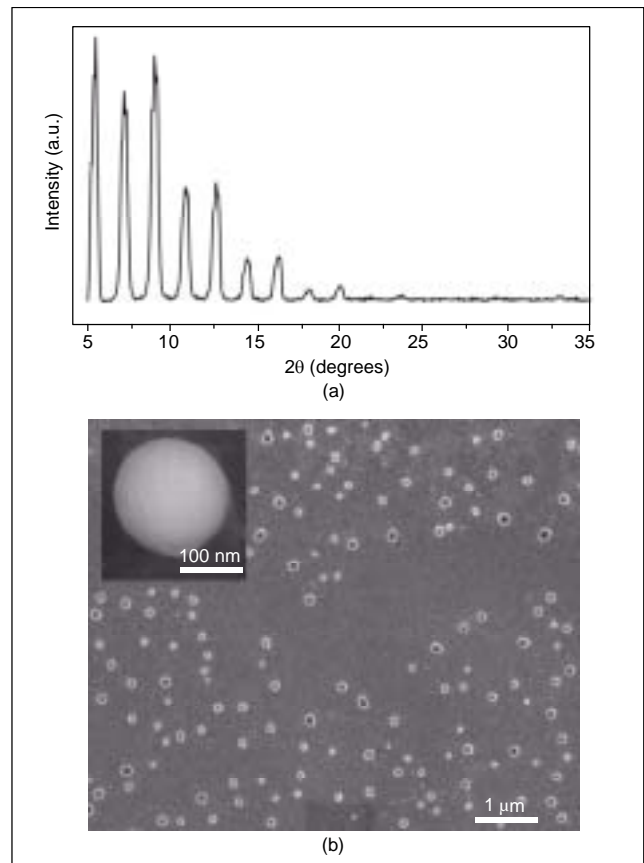


Fig. 6. (a) XRD pattern and (b) SEM image of silver stearate grown on 4-MBA-capped Au nanoparticles. The magnified image shows a single particle.

the mixture of nanoparticles and AgNO<sub>3</sub> while vigorously stirring. After three hours, we filtered the reddish-white precipitates, washed them several times with methanol, and finally dried them in a vacuum. Figure 6(a) shows the XRD pattern of the reddish-white precipitates. The well-defined progression of intense peaks seen in Figs. 1(b) and 3(a) clearly indicates the formation of layered silver stearate. On the other hand, Fig. 6(b) shows a SEM image of the reddish-white precipitates; the precipitates are spherical with sizes ranging from about 80 to 100 nm. We are currently attempting to fabricate these hybrid nanoparticles in a much narrower size distribution, presuming that such uniform particles may function as photonic bandgap materials.

Figure 7(a) shows the IR spectrum of 4MBA-capped Au nanoparticles and Fig. 7(b), the IR spectrum of the precipitates. The carbonyl stretching band observable at about  $1700 \text{ cm}^{-1}$  in Fig. 7(a) is totally absent in Fig. 7(b). The IR spectral feature of the precipitates in Fig. 7(b) is almost the same as that of neat silver stearate; the spectral feature in Fig. 7(b) is also the same as that of the 2D-patterned silver stearate in Fig. 4. These observations indicate that layered silver stearates must have

grown consecutively on the surfaces of the 4-MBA-capped Au nanoparticles. Recalling the interlayer spacing of silver stearate, the measured size of about 100 nm in Fig. 6 should correspond to the formation of about 20 layers of silver stearate on the 4-MBA-capped Au nanoparticles.

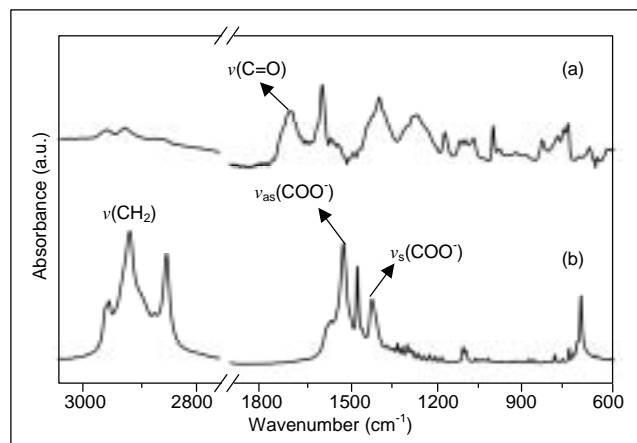


Fig. 7. IR spectra of (a) the as-prepared 4-MBA-capped Au nanoparticles and (b) the silver stearate grown on 4-MBA coated Au nanoparticles.

#### IV. Conclusion

In this work, we have demonstrated that layered silver stearate can be grown in a controlled way on 2D and 3D surfaces by a simple self-assembly process. The method can be applied to the fabrication of microelectronic devices, incorporating, for instance, the 2D conductivity properties of  $\text{AgCO}_2\text{R}$  materials. 3D-photon band gap materials may also be synthesized using nanoparticles for a template. This implies that, if the terminal functionality of the precursor organic monolayers is judiciously chosen, a variety of organic-inorganic hybrid materials can be grown by this method.

#### References

- [1] I.A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P.M. Eisenberger, and S.M. Gruner, "Biomimetic Pathways for Assembling Inorganic Thin Films," *Science*, vol. 273, 1996, pp. 892-898.
- [2] F.W. Matthews, G.G. Waren, and J.H. Michell, "Derivatives of Fatty Acids," *Anal. Chem.*, vol. 22, 1950, pp. 514-519.
- [3] B.P. Tolochko, S.V. Chernov, S.G. Nikitenko, and D.R. Whitcomb, "EXAFS Determination of the Structure of Silver Stearate,  $[\text{AgO}_2\text{C}(\text{CH}_2)_{16}\text{CH}_3]_2$ , and the Effect of Temperature on the Silver Coordination Sphere," *Nucl. Instrum. Meth. A*, vol. 405, 1998, pp. 428-434.
- [4] N.F. Uvarov, L.P. Burleva, M.B. Mizen, D.R. Whitcomb, and C. Zou, "Conductivity of Long-Chain Silver Carboxylates and Their

Thermal Decomposition Products," *Solid State Ionics*, vol. 31, 1998, pp. 31-40.

- [5] K. Abe, T. Hanada, Y. Yoshida, N. Tanigaki, H. Takiguchi, H. Nagasawa, M. Nakamoto, T. Yamaguchi, and K. Yase, "Two-Dimensional Array of Silver Nanoparticles," *Thin Solid Films*, vol. 327, 1998, pp. 524-527.
- [6] S.J. Lee, S.W. Han, H.J. Choi, and K. Kim, "Structure and Thermal Behavior of a Layered Silver Carboxylate," *J. Phys. Chem. B*, vol. 106, 2002, pp. 2892-2900.
- [7] Y. Xia and G.M. Whitesides, "Soft Lithography," *Angew. Chem. Int. Ed.*, vol. 37, 1998, pp. 550-575.
- [8] M.J. Hostetler, A.C. Templeton, and R.W. Murray, "Dynamics of Place-Exchange Reactions on Monolayer-Protected Gold Cluster Molecules," *Langmuir*, vol. 15, 1999, 3782-3789.
- [9] S.R. Johnson, S.D. Evans, and R. Brydson, "Influence of a Terminal Functionality on the Physical Properties of Surfactant-Stabilized Gold Nanoparticles," *Langmuir*, vol. 14, 1998, pp. 6639-6647.
- [10] R.A. MacPhail, H.L. Strauss, R.G. Snyder, and C.A. Elliger, "C-H Stretching Modes and the Structure of *n*-Alkyl Chains. 2 Long, All-trans Chains," *J. Phys. Chem.*, vol. 88, 1984, pp. 334-341.
- [11] R.G. Snyder, H.L. Strauss, and C.A. Elliger, "C-H Stretching Modes and the Structure of *n*-Alkyl Chains. 1. Long, Disordered Chains," *J. Phys. Chem.*, vol. 86, 1982, pp. 5145-5150.
- [12] C. Almirante, G. Minoni, and G. Zerbi, "Mechanism of Solid to Liquidlike Phase Transition of Alkyl Chains in Bilayer Systems. An Infrared Spectroscopic Study of  $[\text{CH}_3(\text{CH}_2)_{13}\text{NH}_3]_2\text{MnCl}_4$  and  $[\text{CH}_3(\text{CH}_2)_{13}\text{NH}_3]_2\text{ZnCl}_4$ ," *J. Phys. Chem.*, vol. 90, 1986, pp. 852-859.
- [13] S.J. Lee and K. Kim, "Diffuse Reflectance Infrared Spectra of Stearic Acid Self-Assembled on Fine Silver Particles," *Vib. Spectrosc.*, vol. 18, 1998, pp. 187-201.



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