

Controlled Assembly of Regular Composite Nanowire Arrays and Their Multilayers Using Electropolymerized Polymers as Templates

J. F. Liu,^{*,†} K. Z. Yang,[‡] and Z. H. Lu[†]

Contribution from the National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing 210096, P. R. China, and Institute of Colloid and Interface Chemistry, Shandong University, Jinan 250100, P. R. China

Received January 16, 1997[⊗]

Abstract: This paper describes a novel chemical method for controlled assembly of regular composite nanowire arrays at the molecular level. The polycationic poly(*N*-vinylcarbazole) (PNVK) template is prepared by electrochemical polymerization of the *N*-vinylcarbazole monomer. Regular composite nanowire arrays of thallic oxide (Tl₂O₃) and polycationic PNVK are fabricated through ordered aggregation of the negative Tl₂O₃ nanoparticles along the positive chains of the polycationic PNVK in the polycationic PNVK–arachidic acid (AA) mixed monolayer on the air–alkaline Tl₂O₃ sol interface. The widths of the Tl₂O₃ and the polycationic PNVK nanowires are 3.2 and 2.7 nm, respectively. The above regular nanowire arrays can also be obtained when a polycationic PNVK single component is used as a template. These nanowires lie in the plane of the corresponding monolayers. The polycationic PNVK–AA mixed monolayer and the Tl₂O₃ nanowire arrays aggregated along the polycationic PNVK chains can be easily transferred onto hydrophobic substrates layer by layer to form Langmuir–Blodgett (LB) multilayers with a spacing of 5.5 nm. This novel method should be applicable to the preparation of a wide range of composite nanowire arrays.

Introduction

In recent years, there has been an increasing interest in the fabrication of metallic nanowires and semiconductor silicon nanostructures using the scanning tunneling microscope (STM)^{1,2} and the atomic force microscope (AFM)³ due to their high resolution. These nanofabrication methods require expensive equipment and high-vacuum conditions for predeposition of metal films and complex procedures. Another research approach concerns surface patterning of self-assembled films with lithographic exposure tools.⁴ Imprint lithography with 25 nm resolution has also been reported.⁵ Recently, Langmuir monolayers on the air/aqueous subphase interface have been utilized as templates for preparation of semiconductor nanoparticulate films.⁶ The presence of a monolayer with a negative surface charge is essential to the formation of sulfide semiconductor particulate films⁷ and electrodeposited silver particles.⁸ Appropriately charged nanoparticle sols dispersed in the subphase could be electrostatically attracted to a positively charged

monolayer surface and, thus, be inserted between LB films.⁹ The electrostatic attraction between a cationic polyelectrolyte and anionic nanoparticles could also be utilized to fabricate self-assembled multilayers.¹⁰ For fabrication of regular nanowire arrays, however, the challenge is how to control the aggregating dimension of nanoparticles in the subphase.

Tl₂O₃ is an n-type degenerate semiconductor with a bandgap of 1.4 eV and a room temperature resistivity of only 70 μΩ·cm.¹¹ In 1990, Switzer et al. reported a novel electrodeposition technique for Tl–Pb oxide superlattices and measured the thickness of each layer by using X-ray diffraction analysis.¹² In 1992, they obtained scanning tunneling microscopic images of cleaved cross-sections of the Tl–Pb oxide superlattices.¹³ In 1994, the same group reported the electrodeposition of Tl₂O₃ defect-chemistry superlattices with layer thicknesses of 6.7 nm.¹⁴ These electrodeposited superlattices have the high carrier density and low electronic dimensionality of high transition temperature superconductors.¹⁵ We have investigated the effect of the electrodepositing current densities on the crystallinity, morphology, and conductivity of the electrodeposited Tl₂O₃ films.¹⁶ We have also studied the characteristics of the mixed monolayers of polycationic PNVK and arachidic acid (AA) on pure water subphase and the resultant multilayers.¹⁷ In the present approach, we prepared regular Tl₂O₃/polycationic PNVK nanowire

* Author to whom correspondence should be addressed.

† Southeast University.

‡ Shandong University.

⊗ Abstract published in *Advance ACS Abstracts*, October 15, 1997.

(1) Rubel, S.; Trochet, M.; Ehrichs, E. E.; Smith, W. F.; deLozanne, A. *J. Vac. Sci. Technol.* **1994**, *B12*, 1894.

(2) Kramer, N.; Birk, H.; Jorritsma, J.; Schonenberger, C. *Appl. Phys. Lett.* **1995**, *66*, 1325.

(3) Snow, E. S.; Campbell, P. M.; McMar, P. J. *Appl. Phys. Lett.* **1993**, *63*, 7749.

(4) Calvert, J. M. *J. Vac. Sci. Technol.* **1993**, *B11*, 2155. Abbot, N. L.; Folkers, J. P.; Whitesides, G. M. *Science* **1992**, *257*, 1380. Lopez, G. P.; Biebuyck, H. A.; Frisbie, D. C.; Whitesides, G. M. *Science* **1993**, *260*, 647. Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002. Lopez, G. P.; Biebuyck, H. A.; Harter, R.; Kumar, A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 2225. Fodor, S. P. A.; Rozsnyai, L. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 5993.

(5) Chou, S. Y.; Karass, P. R.; Renstrom, P. J. *Science* **1996**, *272*, 85.

(6) Fendler, J. H.; Meldrum, F. C. *Adv. Mater.* **1995**, *7*, 607.

(7) Zhao, X. K.; Xu, S.; Fendler, J. H. *Langmuir* **1991**, *7*, 250.

(8) Yi, K. C.; Horvolgyi, Z.; Fendler, J. H. *J. Phys. Chem.* **1994**, *98*, 3872.

(9) Tian, Y.; Wu, X.; Fendler, J. H. *J. Phys. Chem.* **1994**, *98*, 4913. Furlong, D. N.; Urquhart, R.; Grieser, F.; Tanaka, K.; Okahata, Y. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2031.

(10) Kleifield, E. R.; Ferguson, G. S. *Science* **1994**, *265*, 370.

(11) Shukla, V. N.; Wirtz, G. P., *J. Am. Ceram. Soc.* **1977**, *60*, 253.

(12) Switzer, J. A.; Shane, M. J.; Phillips, R. J. *Science* **1990**, *247*, 444.

(13) Switzer, J. A.; Raffaele, R. P.; Phillips, R. J.; Hung, C.-J.; Golden, T. D. *Science* **1992**, *258*, 1918.

(14) Switzer, J. A.; Hung, C.-J.; Breyfogle, B. E.; Shumsky, M. G.; Leeuwen, R. V.; Golden, T. D. *Science* **1994**, *264*, 1573.

(15) Triscione, J.-M.; Karkut, M. G.; Antognazza, L.; Brunner, O.; Fischer, O. *Phys. Rev. Lett.* **1989**, *63*, 1016.

(16) Liu, J. F.; Wang, S. X.; Yang, K. Z. *Thin Solid Films* **1997**, *298*, 156.

(17) Liu, J. F.; Wang, S. X.; Yang, K. Z. *Chin. J. Mol. Sci.* **1994**, *12*, 182.

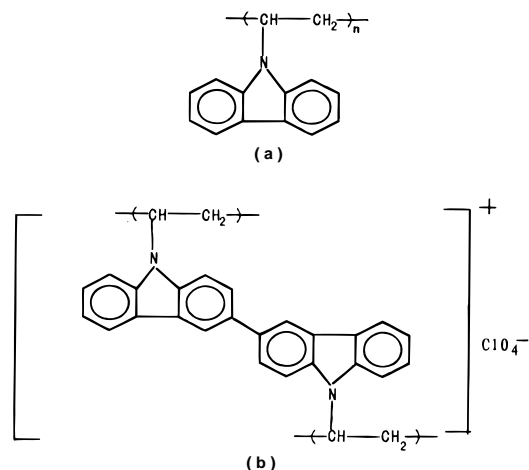


Figure 1. Structural formula of poly(*N*-vinylcarbazole): (a) radically polymerized poly(*N*-vinylcarbazole) and (b) electropolymerized poly(*N*-vinylcarbazole).

ires on the air-alkaline Tl_2O_3 aqueous sol interface by using the electropolymerized PNVK as a template.

Experimental Section

Preparation of Poly(*N*-vinylcarbazole). (a) **Free Radical Polymerization.** *N*-Vinylcarbazole (Fluka, purity >95%) was recrystallized from methanol followed by drying in vacuum at ambient temperature. Benzene was dried with 4 Å molecular sieves. According to ref 18, radical polymerization was performed in a benzene solution of 20 cm³ containing 2.0 g of *N*-vinylcarbazole monomer and 0.08 g of azobisisobutyronitrile as the radical initiator. The reaction mixture was refluxed for 10 h at 80 °C, then cooled to room temperature followed by reprecipitation from the benzene solution into 60 cm³ of methanol. This procedure was repeated three times. The resultant product was dried in vacuum at ambient temperature. Its structure is shown in Figure 1a.

(b) **Electrochemical Polymerization.** Sodium perchlorate was dried in vacuum at 140–160 °C. Benzene was dried by 4 Å molecular sieves. The polycationic PNVK was prepared by electrochemical polymerization of the monomer on a platinum electrode which had been pretreated by heating in an alcohol flame to remove organic residues. The counter and the reference electrodes were platinum and saturated calomel electrodes (SCE). Polymerization was performed at +1.20 V in an acetonitrile solution of 20 mmol·dm⁻³ *N*-vinylcarbazole and 0.50 mol·dm⁻³ sodium perchlorate under electromagnetic stirring. The electropolymerized PNVK film on the platinum electrode was rinsed with acetonitrile, dissolved in dimethylformamide (DMF). The resultant PNVK solution was filtered, concentrated by vacuum distillation, and dried under vacuum at 100 °C. The structural representation of the electropolymerized PNVK is shown in Figure 1b.

Infrared (IR) Spectrum Analysis. IR spectra were recorded on a NICOLET FT-IRDX spectrophotometer (KBr pellet).

Preparation of Tl_2O_3 Sol Subphase. The Tl_2O_3 (**Caution:** thallium compounds are extremely toxic.) aqueous sol subphase was prepared by reaction of thallic oxide with sulfuric acid until the solution became transparent and colorless. Then the pH of the solution was adjusted to 12 with potassium hydroxide to assure that the Tl_2O_3 nanoparticles be negatively charged by adsorption of OH^- anions. During the preparation process of the Tl_2O_3 colloidal subphase, the solution turned from colorless to brown at pH = 1.5, indicating the formation of Tl_2O_3 colloids. The concentration of Tl_2O_3 was 2.2×10^{-5} mol/L. Deionized, twice-distilled water was used to prepare the subphase.

Measurement of Surface Pressure (π)-Area (A) Isotherms and Deposition of LB Multilayers. Measurement of π -A isotherms were performed at 26 °C in a British NIMA system with a 2000 round trough. The spreading solution was $CHCl_3$ -dimethylformamide ($v:v = 1:1$) containing 0.060 mg/mL of polycationic PNVK. Ten minutes after spreading, the film was compressed at a rate of 30 cm²/min. Deposition

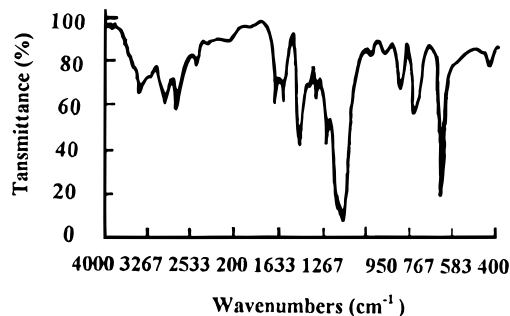


Figure 2. Infrared spectrum of electropolymerized poly(*N*-vinylcarbazole).

of polycationic PNVK-AA (AA was spectroscopic grade) multilayers was carried out at a dipping rate of 10 mm/min and at π of 25 mN/m (variation of π was kept within 0.5 mN/m by a computer-controlled system during the transfer process). The time interval between two consecutive layers was 10 min. The hydrophobic treatment of the substrate was as follows: (a) clean with chloroform, (b) immerse in a hot chromic acid mixture for 2 h and then rinse thoroughly with deionized, twice-distilled water, (c) keep in 4% sodium hydroxide solution for 12 h, (d) rinse thoroughly with deionized, twice-distilled water again, and (e) immerse in 5% trimethylchlorosilane for 10 min and then clean with chloroform. Six, nine, and fifteen layers were transferred onto the hydrophobic glass substrate.

Small-Angle X-ray Diffraction Analysis (SAXRD). SAXRD curves were recorded on a Rigaku D/Max- γ A X-ray diffractometer with Cu K α radiation ($\lambda = 0.154$ nm). The acceleration voltage is 40 kV, the tube current is 100 mA, and the scan rate is 1 deg/min.

Transmission Electron Microscopy (TEM). TEM images were obtained on a JEM-100 CXII transmission electron microscope (100 kV). Ten minutes after spreading, the film was compressed at a rate of 30 cm²/min. Thirty minutes after the polycationic PNVK-AA monolayers were compressed to 25 mN/m, the monolayer was transferred onto a Formvar-coated, 230 mesh copper grid by vertical dipping.

Results and Discussion

Structure of Electropolymerized PNVK. The IR spectrum of the electropolymerized material is shown in Figure 2. The maxima at 800 and 880 cm⁻¹ indicate the presence of 1,2,4-trisubstituted benzene rings. The pronounced maximum at 1100 cm⁻¹ is due to the incorporated perchlorate anions. The IR spectrum indicates that 3,3'-dicarbazyl structure is formed. The structure of the electropolymerized PNVK is shown in Figure 1b. This structure is consistent with that deduced from the electrochemical analysis.¹⁹ The structure of radically polymerized PNVK (Figure 1a) and the electropolymerized one (Figure 1b) are different. The radically polymerized PNVK chains are neutral, while the electropolymerized ones are positive. It is reasonable that the polycationic chains of the electropolymerized PNVK would adsorb negative nanoparticles in the subphase.

Characteristics of π -A Isotherms. Behavior of the polycationic PNVK template on the surface of the subphase was examined by π -A isotherms. The polycationic PNVK could not form stable monolayers whether on the water or on the alkaline Tl_2O_3 sol subphase. However, it could form stable mixed monolayers with arachidic acid. Five minutes after the monolayer was compressed to the target surface pressure of 25 mN/m, the area of the monolayer decreased by only 0.2%, indicating a high stability of the mixed monolayer on the

(19) Dubois, J. E.; Desbene-Monvernay, A.; Lacaze, P. C. *J. Electroanal. Chem.* **1982**, 132, 177. Desbene-Monvernay, A.; Dubois, J. E.; Lacaze, P. C. *J. Electroanal. Chem.* **1985**, 189, 51. Compton, R. G.; Davis, F. J.; Grant, S. C. *J. Appl. Electrochem.* **1986**, 16, 239. Desbene-Monvernay, A.; Lacaze, P. C.; Delamar, M. *J. Electroanal. Chem.* **1992**, 334, 241.

(18) Ellinger, L. P. *J. Appl. Polym. Sci.* **1965**, 9, 3939.

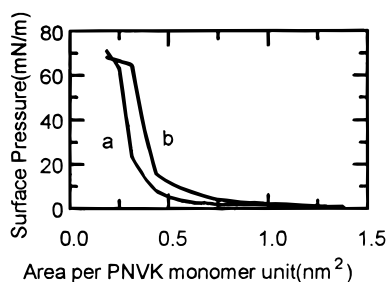


Figure 3. Surface pressure (π)-area (A) isotherms (26 °C) of polycationic PNVK-AA (molar ratio = 1:1) monolayers: (a) deionized, twice-distilled water subphase; (b) aqueous Tl_2O_3 (2.2×10^{-5} mol/L) sol subphase (pH = 12). Compression speed: 30 cm^2/min .

subphase. So use of AA thus promotes the formation of the monolayer and also increases its stability. Figure 3 shows the π - A isotherms of the polycationic PNVK-AA mixed monolayer on a pure water subphase (curve a) and on an aqueous Tl_2O_3 sol subphase with a pH of 12 (curve b). The mixed monolayer has the steepest solid-like region with a collapse pressure higher than 60 mN/m. By extrapolating the steepest solid-like region we can obtain the limiting area per PNVK monomer unit (A_0). For the Tl_2O_3 aqueous sol subphase (pH = 12), A_0 is 0.20 nm^2 . This value is larger than 0.16 nm^2 , the value of A_0 corresponding to the pure water subphase. According to the CPK (Corey-Pauling-Koltun) model, the PNVK monomer unit is a cuboid.²⁰ The smallest face area of it is 0.18 nm^2 . The measured limiting area per PNVK monomer unit on the Tl_2O_3 aqueous sol subphase 0.20 nm^2 is close to 0.18 nm^2 , the smallest face area of the CPK model of the PNVK monomer unit. This result demonstrates that the polycationic PNVK chains lie horizontally on the Tl_2O_3 sol subphase. The difference in the value of A_0 indicates that the polycationic PNVK is dispersed more easily on the Tl_2O_3 aqueous sol subphase than on the pure water subphase. This can be the electrostatic attraction between the polycationic PNVK chains and the negatively charged Tl_2O_3 nanoparticles.

Tl_2O_3 /PNVK Composite Nanowire Arrays. Formation of regular nanowire arrays in the plane of the polycationic PNVK-AA mixed monolayers was confirmed by the transmission electron microscopic (TEM) examinations. TEM images are shown in Figure 4. Because thallium is a heavy element, the black lines represent the Tl_2O_3 nanowires. The polycationic PNVK contains C, H, O, and N light elements. So the white lines represent the polycationic PNVK chains. These nanowire arrays lie in the plane of the polycationic PNVK-AA mixed monolayers. From the TEM images, the widths of the Tl_2O_3 and polycationic PNVK nanowires are estimated to be about 3.2 and 2.7 nm, respectively. The initially observed nanowire array patterns were in much better order than those in Figure 4. The defects in the TEM images resulted from electron beam damage during the photographic exposure. Similar to previous reports,²¹ the minimum dose conditions were used during the observation and the imaging process to obtain the maximum amount of structural information before the films degraded in the electron beam. Kramer et al. have fabricated Ta-Ir nanowires by employing a STM and a high-vacuum system as well as a series of procedures.² Snow et al. have obtained silicon nanostructure with an AFM and an electron cyclotron resonance source.³ The width of the Tl_2O_3 nanowire is only one-thirteenth that of the Ta-Ir nanowire width fabricated by using STM² and one-third of the Si nanowire width formed using AFM.³

At pH 9, regular nanowire arrays were still formed. No nanowires were observed at pH 5. For single polycationic PNVK component films on the Tl_2O_3 aqueous sol subphase (pH 12), regular nanowire array patterns similar to those in Figure 4a-c were observed and the pH dependence was identical to that of the polycationic PNVK-AA mixed templates. In addition, formation of the nanowire arrays was not the result of surface pressure. When no surface pressure was applied, nanowire arrays were still observed whether the polycationic PNVK or the polycationic PNVK-AA templates were used. The surface pressure compresses the monolayer into a dense one.

Formation of regular nanowire arrays is attributed to the adsorption of the negatively charged Tl_2O_3 nanoparticles in the subphase along the polycationic PNVK chains. During the preparation process of the Tl_2O_3 colloidal subphase, the solution turned from colorless to brown at pH = 1.5, which indicated the formation of the Tl_2O_3 nanoparticles. For the acidic subphase, the concentration of H^+ ions was high. The Tl_2O_3 nanoparticles are positively charged due to adsorption of H^+ ions. The composite nanowires could not be formed due to the electrostatic repulsion between the positively charged chains and the positively charged Tl_2O_3 nanoparticles. When the subphase was alkaline, however, the concentration of OH^- ions was higher. The Tl_2O_3 nanoparticles are then negatively charged, due to the adsorption of OH^- ions. In that case, Tl_2O_3 /polycationic PNVK nanowire arrays were formed. For AA monolayers prepared under the same conditions as the above polycationic PNVK-AA mixed monolayers, no nanowire patterns were observed. Unlike the polycationic PNVK, the AA molecules would be negative due to reaction of the head group of the arachidic molecules with the OH^- ions in the subphase. The resultant carboxylic anions of the AA molecules and the negatively charged Tl_2O_3 colloidal particles would electrostatically repel each other. In the case of the radically polymerized PNVK-AA mixed monolayers on the Tl_2O_3 colloidal subphase (pH = 12), TEM images in Figure 4d demonstrated that aggregates with a size of hundreds of nanometers were formed. No nanowires were observed. From Figure 1a it can be seen that the chains of the radically polymerized PNVK are neutral. So there is no electrostatic attraction between the polymer chains and the Tl_2O_3 nanoparticles. Similar to radically polymerized polythiophene,²² the radically polymerized PNVK aggregates easily. These results demonstrate that the electrostatic attraction is responsible for the formation of the Tl_2O_3 /polycationic PNVK nanowire arrays. By using the electrodeposition technique, Switzer et al. have obtained thallium oxide superlattices discernible over a 1-2 μm STM scan range.¹⁴ In our case, ordered adsorption of negative Tl_2O_3 nanoparticles along the polycationic PNVK chains resulted in the formation of Tl_2O_3 /polycationic PNVK composite nanowire arrays.

Polycationic PNVK-AA LB Multilayers Containing Tl_2O_3 /Polycationic PNVK Nanowire Arrays in the Plane of Each Layers. The polycationic PNVK template on the air-alkaline Tl_2O_3 sol interface cannot be transferred successfully to form LB multilayers because the transfer ratios are irregular. The transfer ratio is often used as a measure of the quality of deposition. It is defined as the ratio of the area of monolayer removed from the subphase surface to the area of substrate coated by the monolayer. Irregular transfer ratios are almost always a sign of unsatisfactory film deposition. The polycationic PNVK-AA mixed monolayers with regular nanowire arrays in its plane on the air-alkaline Tl_2O_3 sol interface,

(22) Watanabe, I.; Hong, K.; Rubner, M. F. *Thin Solid Films* **1989**, 179, 221.

(20) Miyashita, T.; Yatsue, T. *J. Phys. Chem.* **1991**, 95, 2448.

(21) Freyer, J. R.; Hann, R. A.; Eyres, B. L. *Nature* **1985**, 313, 382. Uyeda, N.; Takenaka, T.; Aoyama, K.; Matsumoto, M.; Fujiyoshi, Y. *Nature* **1987**, 327, 319.

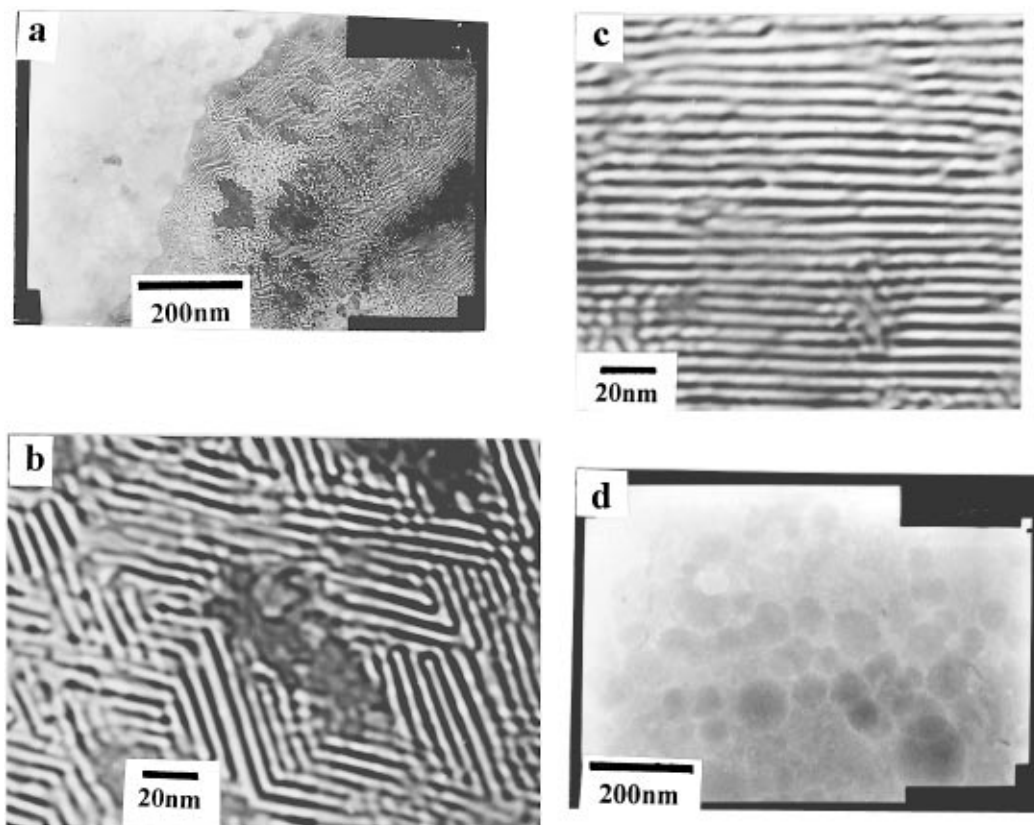


Figure 4. (a) TEM image of composite Ti_2O_3 /polycationic PNVK nanowire arrays in the plane of polycationic PNVK-AA (molar ratio = 1:1) monolayers. (b and c) Enlarged TEM images of composite Ti_2O_3 /polycationic PNVK nanowire arrays. (d) TEM image of radically polymerized PNVK-AA (molar ratio = 1:1) monolayers. Surface pressure (π): 25 mN/m. Subphase: Ti_2O_3 (2.2×10^{-5} mol/L) sol subphase (pH = 12).

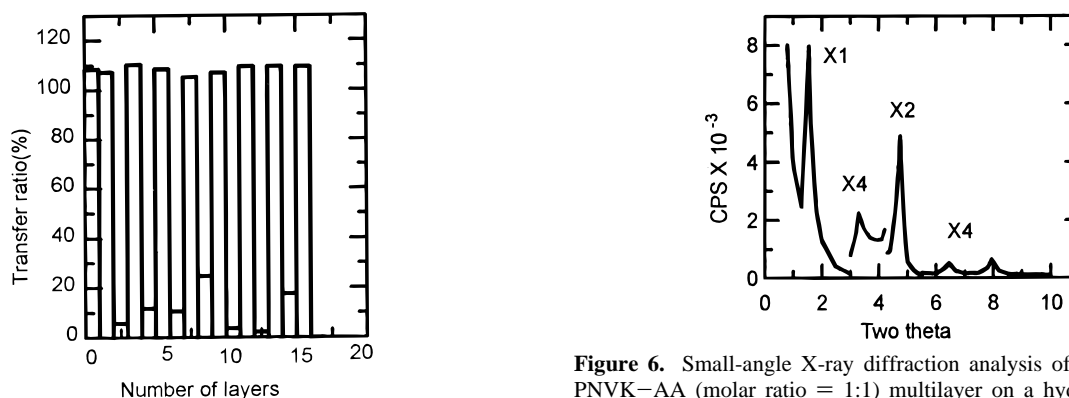


Figure 5. Variation of transfer ratios with number of deposition layers of polycationic PNVK-AA (molar ratio = 1:1) mixed monolayers. Subphase: Ti_2O_3 (2.2×10^{-5} mol/L) sol subphase (pH = 12). Surface pressure (π): 25 mN/m. Dipping rate: 10 mm/min.

however, can be easily transferred onto hydrophobic substrates, layer by layer to form LB multilayers. Use of AA is necessary for the successful transfer of the polycationic PNVK-AA mixed monolayer. The relationship between the transfer ratio and the number of deposited layers is shown in Figure 5. The even layers had a transfer ratio of 1.1, while the odd layers had a transfer ratio ranging between -0.2 and 0.2 except the first layer. Generally there are three deposition modes, X, Y, and Z.^{23a} When a substrate is moved through the monolayer on the subphase surface, the monolayer can be transferred during upstroke or downstroke. For the Y-type deposition mode, the

Figure 6. Small-angle X-ray diffraction analysis of a polycationic PNVK-AA (molar ratio = 1:1) multilayer on a hydrophobic glass substrate. Subphase: Ti_2O_3 (2.2×10^{-5} mol/L) sol subphase (pH = 12). Surface pressure (π): 25 mN/m. Dipping rate: 10 mm/min.

monolayer is transferred in both the upstroke and downstroke. For the X-type deposition mode, the monolayer only transferred in downstroke. When the monolayer transferred only in upstroke, the deposition mode is referred as Z-type. From Figure 5, it can be seen that the deposition mode of the polycationic PNVK-AA monolayers is type Z. SAXRD (small-angle X-ray diffraction) techniques have been used extensively to determine the spacing of LB multilayers.^{23b} Figure 6 shows the SAXRD curve of the polycationic PNVK-AA LB multilayer on a hydrophobic glass substrate. Five diffraction peaks are observed. According to the Bragg's equation, the peak at $2\theta = 1.55^\circ$ corresponds to a spacing of 5.7 nm. Similarly, the higher-order reflections at 3.33° , 4.72° , 6.42° , and 7.96° correspond to spacings of 5.3, 5.6, 5.5, and 5.5 nm, respectively. The average spacing is 5.5 nm. This value is equal to twice the length of the hydrocarbon chains of the arachidic acid molecules,²⁴ indicating that the hydrocarbon

(23) (a) Pettey, M. C. In *Langmuir-Blodgett Films*; Roberts, G., Ed.; Plenum: New York, 1990; Chapter 4, pp 93–8. (b) Pettey, M. C. In *Langmuir-Blodgett Films*; Roberts, G., Ed.; Plenum: New York, 1990; Chapter 4, pp 137–140.

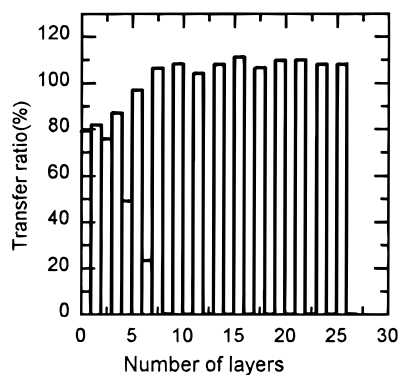


Figure 7. Variation of transfer ratios with number of deposition layers for AA monolayers. Subphase: Ti_2O_3 (2.2×10^{-5} mol/l) sol subphase (pH = 12). Surface pressure (π): 25 mN/m. Dipping rate: 10 mm/min.

chains of the arachidic acid molecules are oriented at right angles to the hydrophobic glass substrate. The multilayer used for the SAXRD analysis was formed using nine layer by layer transfers from the polycationic PNVK-AA mixed monolayer on the air-alkaline Ti_2O_3 sol interface. For the film formed with 15 layers, the peak height increased, but the peak position was unchanged. For the film formed with 5 layers, the peaks centered at $2\theta = 3.33^\circ$, 6.42° , and 7.96° disappeared and the peak height at $2\theta = 1.55^\circ$ and 4.72° decreased. The peak positions did not change. The above SAXRD analysis indicates that well-layered structures of the polycationic PNVK-AA LB multilayers are formed and the hydrocarbon chains of the arachidic acid molecules are vertical to the glass substrate. It is evident that the polycationic PNVK-AA LB multilayer structure was controlled by the AA molecules. In addition, the relationship between the transfer ratio and the number of deposited layers in Figure 5 indicates a spacing of 2.7 nm, the length of the hydrocarbon chains of the AA molecules.²⁴ In fact, the spacing determined by the SAXRD (Figure 6) is 5.5 nm. So it is estimated that the AA molecules in the polycationic PNVK-AA mixed monolayers overturn during the deposition process, thus leading to the formation of Y-type LB multilayers. We fabricated pure AA LB multilayers to obtain the relationship between the deposition ratios and the number of deposition layers. SAXRD analysis was also performed to get the layer spacing of the AA LB multilayers. The relationship between the transfer ratio and the numbers of deposited layers is shown in Figure 7 for AA LB multilayers prepared under the same conditions as above. Evidently, the deposition process undergoes a transformation from a Y-type to a Z-type deposition mode at the fifth layer. The corresponding SAXRD result is shown in Figure 8, where seven diffraction peaks are observed at 1.54° , 3.17° , 4.75° , 6.37° , 7.98° , 9.54° , and 11.20° . From these seven diffraction peaks, the spacings were calculated to be 5.7, 5.6, 5.6, 5.6, 5.5, 5.6, and 5.5 nm. The average value was 5.6 nm, indicating a Y-type AA LB multilayer structure. So the AA molecules must have overturned during the transfer process, resulting in the formation of a Y-type AA LB multilayer with

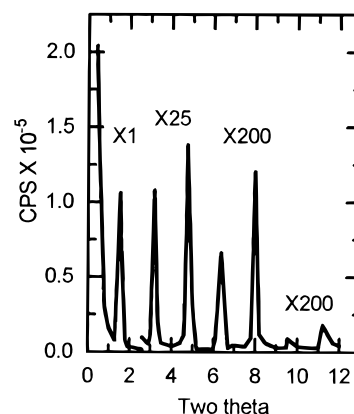


Figure 8. Small-angle X-ray diffraction analysis of an AA multilayer on a hydrophobic glass substrate. Subphase: Ti_2O_3 (2.2×10^{-5} mol/L) sol subphase (pH = 12). Surface pressure (π): 25 mN/m. Dipping rate: 10 mm/min.

a spacing of twice the length of the hydrocarbon chains of the AA molecules. This result is consistent with the earlier studies of long-chain aliphatic acid salts on the surface of a high-pH subphase.²⁵ It is reasonable that the AA molecules in the polycationic PNVK-AA mixed monolayer overturn during the deposition process, thus leading to the formation of Y-type multilayers containing Ti_2O_3 /polycationic PNVK nanowire arrays in the plane of each layer.

Conclusion

In conclusion, controlled assembly of regular Ti_2O_3 /polycationic PNVK composite nanowire arrays is realized on the air-alkaline Ti_2O_3 sol subphase interface by using polycationic PNVK as a template. The polycationic PNVK is prepared by electrochemical polymerization of the *N*-vinylcarbazole monomer. The widths of the Ti_2O_3 and the polycationic PNVK nanowires are 3.2 and 2.7 nm, respectively. These nanowire arrays lie in the plane of the polycationic PNVK-AA monolayers. The electrostatic attraction between the positive chains of the polycationic PNVK template and the negative Ti_2O_3 nanoparticles in the subphase is essential to the formation of the regular Ti_2O_3 /polycationic PNVK composite nanowire arrays. The polycationic PNVK-AA monolayer with regular nanowire arrays in its plane can be easily transferred onto hydrophobic substrates layer by layer to form LB multilayers with a spacing of 5.5 nm. As compared with the STM and AFM techniques, formation of composite nanowire arrays on the air-aqueous sol interface is relatively simple, convenient, and inexpensive, and the resolution of the nanowires is at the molecular level. Electrochemical polymerization is a useful method for preparation of a wide range of positively charged conducting polymers such as polyaniline, polypyrrole, and polythiophene from the corresponding monomers.²⁶ The present approach, then, should be applicable to the controlled assembly of a wide range of regular semiconductor/polyionic polymer nanowire arrays and their multilayers.

Acknowledgment. This work was supported by the National Natural Science Foundation of P. R. China and the State Major Basic Project.

JA9701321

(24) Leuthe, A.; Chi, L. F.; Riegler, H. *Thin Solid Films* **1994**, *243*, 351.

(25) Honig, E. P.; Hengst, J. H. P.; Den Engelsen, D. *J. Coll. Interface Sci.* **1973**, *45*, 92.

(26) Diaz, A. F.; Rubinson, J. F.; Mark, H. B., Jr. In *Advances in Polymer Science*; Springer-Verlag: Berlin, Heidelberg, 1988; Vol. 84, pp 113-139.