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pH-Dependent Intercalation of Gold Nanoparticles into a Synthetic Fluoromica Modified with Poly(Allylamine)

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The intercalation of poly(allylamine) (PAA) into a synthetic fluoromica (Na-TSM) was studied in order to understand the subsquent process of gold nanoparticle intercalation into the interlayer galleries. The composition and structure of the PAA intercalation compound (PAA/Na-TSM) was strongly influenced by the pH of its synthesis. At pH 3.0, the fully protonated form of the polymer was intercalated as a single layer (d = 1.42–1.46 nm), accompanied by 0.2–0.4 chloride ions per PAA monomer unit. The role of chloride appears to be to screen the electrostatic repulsion of polycations within the gallery. At pH 12.0, a partially protonated form of PAA intercalates as an expanded layer (d = 1.50–1.61 nm) with no chloride ions. From equilibrium PAA adsorption data, the standard free energy for PAA intercalation at pH 12.0 was –35 kJ/mol. At pH 3.0 and low PAA loading, the corresponding $\Delta G°$ is –64 kJ/mol, consistent with the stronger interaction of protonated PAA chains with the anionic clay sheets. Au nanoparticles (<10 nm diameter) intercalated into PAA/Na-TSM composites made at pH 12.0, but not those made at pH 3.0. The most effective pH for intercalation of well-dispersed Au nanoparticles was 11.0. ζ potential measurements show that, at pH 11.0, the PAA/Na-TSM and Au colloids have nearly neutral and negative surface charges, respectively. From this result, it was concluded that electrostatic interactions as well as covalent bonding between free amine groups and intercalated Au nanoparticles are important for optimal intercalation. A red shoulder extending from 570 to 730 nm on the plasmon resonance absorption of Au/PAA/Na-TSM was observed and was attributed to close interactions between nanoparticles in adjacent galleries.

Introduction

Over the past two decades, the bottom-up synthesis of nanostructured materials has become one of the most active topics in materials chemistry.[1–6] Nanoscale sheets derived from layered inorganic solids are useful building blocks of these assemblies because of their high surface area and the broad range of available chemical compositions.[3,4,6] These solids include polysilicates, layered double hydroxides, layered perovskites, layered transition metal oxides, metal phosphates, metal chalcogenides, graphitic carbons, and other lamellar materials. Colloidal metal nanopatricles are also interesting building units from which to create ordered and complex materials. Among these, gold nanoparticles have been intensively studied because of their unique optical[7] and catalytic properties,[7,8] as well as their biomedical applications.[7,9] In these applications, it is very important to be able to control the size, shape, and dispersion of the nanoparticles on a chemically diverse range of supports. Metal oxides are among the most interesting support materials for gold nanoparticles, especially for plasmonic[10] and catalytic applications.[11] However, in most of these studies, gold nanoparticles have been formed *in situ*, and it has been difficult to control their morphology and dispersion on the oxide supports. So far,

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there have been only a few reports of gold-layered inorganic nanocomposites made from preformed nanoparticles.[12] Kim and Osterloh showed that individual sheets of the exfoliated layered perovskite, $HCa_2Nb_3O_{10}$, could be decorated with gold nanoparticles by grafting (3-aminopropyl)trimethoxysilane to the sheets.[12] In that study, the morphology and dispersion of the nanoparticles could be controlled, but active hydroxyl groups were needed to anchor the silane reagent to the sheets.

The sequential adsorption of oppositely charged polyelectrolytes[4,13] or nanoparticles[2,4,5] as building units, which is called the layer-by-layer (LbL) assembly technique, is a simple but powerful way to construct functional nanostructured materials. The key principle in LbL assembly is the overcompensation of the surface charge in each adsorption step. By adapting this principle to intercalation compounds, we recently showed that it is possible to invert the charge of anionic layered hosts by intercalating an excess of low charge density polycations. Host solids modified in this way become anion exchangers, as demonstrated by the intercalation of a bulky anionic dye into a modified fluoromica.[14] Subsequently, we extended this idea to the intercalation of well-dispersed gold nanoparticles into the galleries of layered anionic hosts (a synthetic fluoromica and Dion–Jacobson-type layered perovskite) through intercalation of a basic polyelectrolyte, poly(allylamine) (PAA), which contains excess primary amine groups.[15] This method seems quite general for dispersing metal nanoparticles on supports because applicable surfaces have to bear only enough negative charge to bind the polymer. However, little is known about the details of the intercalation process, especially the relative importance of electrostatic interactions between the nanoparticles and the modified host.

In order to better understand the driving force for nanoparticle intercalation and the limitations of the synthetic method, we report here a more detailed study of the effects of pH and polymer/host ratio on the reaction. We first studied the adsorption behavior of PAA into a synthetic fluoromica (sodium fluortetrasilisic mica; Na-TSM) as a function of pH and solution composition. Next, the intercalation behavior of gold nanoparticle into the PAA/Na-TSM composites was investigated. In nanoparticle intercalation, the particle size as well as the covalent and electrostatic interactions between the host and the guest are important. Finally, a unique optical property of obtained Au/PAA/Na-TSM nanocomposites will also be reported.

Experimental Section

Materials. Na-TSM with the chemical formula $Na_{0.66}Mg_{2.68}(Si_{3.98}Al_{0.02})O_{10.02}F_{1.96}$ and a cation exchange capacity (CEC) of 120 mequiv/100 g (ME-100, CO-OP Chemicals) was used as received. Na-TSM is a synthetic 2:1-type layered silicate formed by a unique intercalation reaction of talc and Na_2SiF_6.[16] Poly(allylamine hydrochloride) (MW: 15 000, abbreviated as PAA) was obtained from Sigma-Aldrich. Hydrogen tetrachloroaurate(III) ($HAuCl_4 \cdot 3H_2O$, 99.999%) was obtained from Alfa Aesar. Tetrakis(hydroxymethyl)phosphonium chloride (THPC; 80% solution in water) was obtained from Sigma-Aldrich. Water was deionized using a Nanopure water purification system. All compounds were used as received. All glassware was first cleaned in a base bath (saturated KOH/*iso*-propanol solution) and rinsed with water and then immersed in aqua regia (3:1 v/v concentrated HCl/HNO_3) solution, followed by rinsing with copious amount of deionized water. (*Caution*: aqua regia is very corrosive.)

Intercalation of PAA into Na-TSM. Na-TSM (0.75 g) was added to 74.25 g of water, and the suspension was stirred overnight at ambient temperature to ensure the adequate exfoliation of Na-TSM. PAA aqueous solutions at appropriate concentrations (25 g) were added to the exfoliated Na-TSM suspension, and the pH of the suspension was adjusted to 12.0–12.1 or 3.0–3.1 using 10 N aqueous NaOH or 1 N aqueous HCl solution, followed by vigorous agitation for one day. The amount of PAA in the reaction mixture varied: 0.09 (0.1/1), 0.18 (0.2/1), 0.27 (0.3/1), 0.45 (0.5/1), 0.9 (1/1), 2.7 (3/1), 4.5 (5/1), 9.0 (10/1), and 13.5 (15/1) mmol. The numbers in parentheses indicate the ratio of the number of equivalents of PAA to the CEC of the Na-TSM in the suspension. After the reaction, the solid product was separated by centrifugation and washed twice with 100 g of water at each preset pH to remove the excess polymer. Finally, the sample was dried at 333 K for 1 or 2 days and ground to a powder. The intercalation compounds obtained in this way are designated PAA/Na-TSM (*n*), where *n* denotes the initial equivalent ratio of PAA to the CEC of Na-TSM used in the synthesis.

In order to determine the effect of pH changes on intercalated PAA, PAA was first intercalated at pH 12.0–12.1 as described above. During the washing steps, the pH of the suspensions was adjusted with 10 N NaOH or 1 N HCl to 3.0–3.1, 4.0–4.1, 5.0–5.1, 6.0–6.1, 7.0–7.1, 8.0–8.1, 9.0–9.1, 10.0–10.1, 11.0–11.1, or 12.0–12.1.

Synthesis of Au Nanoparticles. Au nanoparticles were prepared as described by Pham et al.[17] To 45 mL of water was added 0.5 mL of 1 M aqueous NaOH solution and 1.0 mL of 0.96 wt % fresh THPC aqueous solution, and the mixture was stirred for 10 min. (To fully activate THPC in the solution, stirring for 10 min prior to adding the $HAuCl_4$ solution is important.) With vigorous stirring of the solution, 1.5 mL of 1.0 wt % aqueous $HAuCl_4$ solution was added quickly, followed by vigorous stirring for 30 min, and this resulted in a deep brown solution. Au nanoparticles synthesized under these conditions are hereafter abbreviated Au(S). From transmission electron microscope (TEM) image analysis (see Supporting Information, Figure S3a), the average diameter of the Au(S) particles was 1.6 ± 0.3 nm. To obtain larger Au nanoparticles, denoted as Au(L), the amount of 1 wt % $HAuCl_4$ solution was increased to 3.0 mL. The Au(L) particle size distribution was estimated to be 2–6 nm from TEM images. In addition, in the preparation of Au(L), the particle size critically depended on the volume of the reaction solution, resulting in extra-large Au nanoparticles [10−20 nm diameter (Au(XL)] on a 6-fold scale. In contrast, for Au(S), the scale of the synthesis can be increased 10-fold without an obvious change in the product particle size distribution.

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Intercalation of Au Nanoparticles into PAA/Na-TSM at Different Au Loadings. In this section, the procedure for Au(S) intercalation is described as representative. Na-TSM (0.75 g) was added to 74.25 g of water, and the suspension was stirred for 1 day at room temperature. A total of 25 g of aqueous PAA solution (180 mM), which is 5 times the CEC, was then added, and the pH of the suspension was adjusted to 12.0–12.1 using 10 N NaOH, followed by vigorous agitation for 1 day. After the reaction, the product was centrifuged and washed twice with 100 g of water at pH = 12.0–12.1 to remove the excess polymer. The wet PAA/Na-TSM so obtained was redispersed in water (75 g in total); 15 g of this suspension was added to an appropriate amount of a Au(S) nanoparticle suspension at pH 10.5–11.5 and stirred for 2 h at room temperature. The pH of the reaction suspension varied according to the amount of Au(S) suspension used. After the nanoparticle intercalation reaction, the suspension was centrifuged, and the solid product was washed three times with water. Finally, the sample was dried at 333 K for 1 or 2 days and ground to a powder. Au(S) intercalation compounds are abbreviated Au(S)/PAA/Na-TSM (*m*), where *m* denotes the actual loading of Au in the product, in millimoles per gram of Na-TSM. The loading was estimated in two different ways: one was by UV–vis absorption spectra of the supernatant solution after the reaction, to confirm complete intercalation in the cases where the supernatant was colorless; the other was from absorption spectra of 6.25×10^{-2} wt % of Au/PAA/Na-TSM when some Au nanoparticles still remained in the supernatant solution after the reaction. The reason that the absorbance of the supernatant could not be used in the second case was because of aggregation of gold in the solution during the reaction. For Au(L) and Au(XL) intercalation, the same procedure was followed, and resulting solids were abbreviated as Au(L) or Au(XL)/PAA/Na-TSM (*m*), respectively.

Intercalation of Au Nanoparticles into PAA/Na-TSM as a Function of pH. The wet PAA/Na-TSM solids, prepared as described above, were suspended in water to a total weight of 75 g. A total of 10 g of this suspension was added to 40 g of water, and the pH of the suspension was adjusted to pH 12.0–12.1, 11.0–11.1, 10.0–10.1, 9.0–9.1, 8.0–8.1, 7.0–7.1, 6.0–6.1, 5.0–5.1, 4.0–4.1, or 3.0–3.1 with aqueous HCl and NaOH solutions. A total of 50 g of a Au(S) nanoparticle suspension (Au content: 3.97×10^{-2} mmol) was then added; the pH was again adjusted to the desired value, and the mixture was stirred for 2 h at room temperature. After the intercalation of the Au nanoparticles, the suspension was centrifuged, and the solid product was washed three times with water at the previously set pH. Finally, the sample was dried at 333 K for 1 or 2 days and ground to a powder.

Instrumentation. X-ray powder diffraction (XRD) patterns were obtained with a Philips X'Pert MPD diffractometer [monochromatized Cu Kα ($\lambda = 0.15418$ nm)]. Infrared spectra were obtained by the KBr pellet method using a Digilab FTS 700 IR spectrometer. Thermogravimetric–mass spectral (TGA-MS) analysis was performed with a TA Instruments TA 2050 attached to a Pfeiffer Thermostar mass spectrometer. UV–vis absorbance and diffuse reflectance spectra were obtained on a Varian/Cary 100 spectrometer. Because we could not completely redisperse PAA/Na-TSM or Au/PAA/Na-TSM after the drying process, wet-gel samples which were washed but not dried were used to obtain UV–vis absorption spectra. For diffuse reflectance measurements, an integrating sphere was used with $BaSO_4$ as a reference. ζ potential measurements were performed with a Brookhaven Instruments Zeta PALS at 298 K. In order to measure the pH dependence of the ζ potential, the pH was adjusted by using 0.01 M aqueous NaOH or HCl solution. TEM images were obtained using a Philips 420 T microscope at an accelerating voltage of 120 kV. Samples for TEM observation were prepared by dropping an aqueous suspension of the wet nanocomposite before drying onto a carbon-coated copper grid and allowing the solvent to evaporate at room temperature. Image analysis to obtain particle size distributions was performed using the public domain software Image J (developed at the U.S. National Institutes of Health and available on the Internet at http://rsb.info.nih.gov/nih-image/). Elemental analysis (C, H, N, and Cl) was performed by Atlantic Microlabs, Inc., Norcross, Georgia.

Results and Discussion

Intercalation of PAA into Na-TSM in High and Low pH. In our previous study,[14a] we briefly investigated the intercalation of PAA into Na-TSM. Here, we investigate the effects of pH on the structure, composition, and surface charge of the resulting intercalation compounds, which influence the intercalation of Au nanoparticles.

Titration of PAA with a strong base shows that, because of a polyelectrolyte effect, there is no sharp equivalence point, and deprotonation occurs over a wide range of pH. In aqueous solution, most of the primary amine groups of PAA are protonated below pH 5.0 and are neutral above pH 11.0.[18] Therefore, in order to investigate the effects of the charge density of PAA chains in the intercalation compounds, PAA was reacted with Na-TSM at pH 3.0 and 12.0. Figure 1 shows XRD patterns of the Na-TSM starting material and PAA/Na-TSM intercalation compounds made under acidic and basic conditions. Figure 2 shows the relationship between the *d*-spacing of PAA/Na-TSM and the PAA loading, as well as the degree of incorporation of chloride ions into PAA/NaTSM. In the XRD pattern of Na-TSM (Figure 1a), two different peaks at *d*-spacing of 1.24 and 0.96 nm were observed as previously reported and are attributed to hydrated and dehydrated layers, respectively.[14,19] Therefore, the basal spacing of the silicate layers was taken to be 0.96 nm.

In the FT-IR spectra of PAA/Na-TSM (5/1) obtained at pH 3.0 (see the Supporting Information, Figure S1a), scissoring vibrational modes of the protonated amine groups (NH_3^+) of PAA were observed at 1633 and 1514 cm^{-1}, and there were no bands that could be attributed to neutral amine groups. This implies that the protonated amine groups of the polymer associate with the negatively charged clay surface or are charge-compensated by intercalated Cl^- ions as $-NH_3^+Cl^-$. When fully protonated PAA was intercalated into Na-TSM at low pH, the basal spacing of PAA/Na-TSM reached 1.42 nm at $n = 0.3/1$ and increased only slightly as *n* was increased to 15/1. Taking into account that the thickness of an extended PAA chain is 0.3–0.5 nm,[20] this means that fully protonated PAA intercalates as a monolayer within the 2D gallery at all values of *n*. The amount of intercalated PAA within the interlayer increased steadily up to *ca.* 1.4 mmol/1 g of clay with an increasing initial

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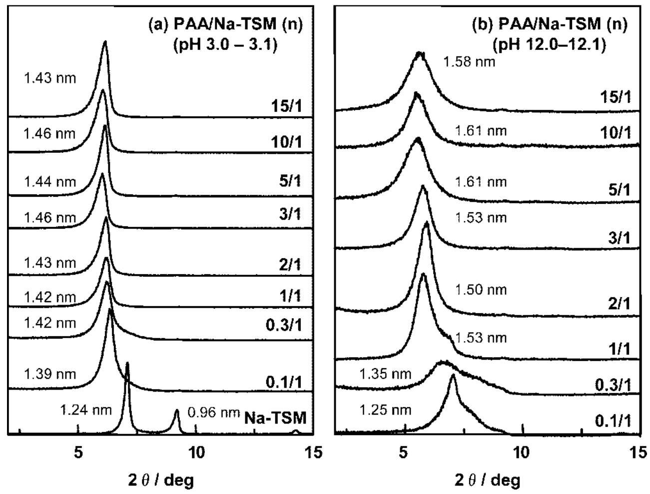

Figure 1. XRD patterns of (a) Na-TSM and PAA/Na-TSM intercalated at pH 3.0 and (b) pH 12.0.

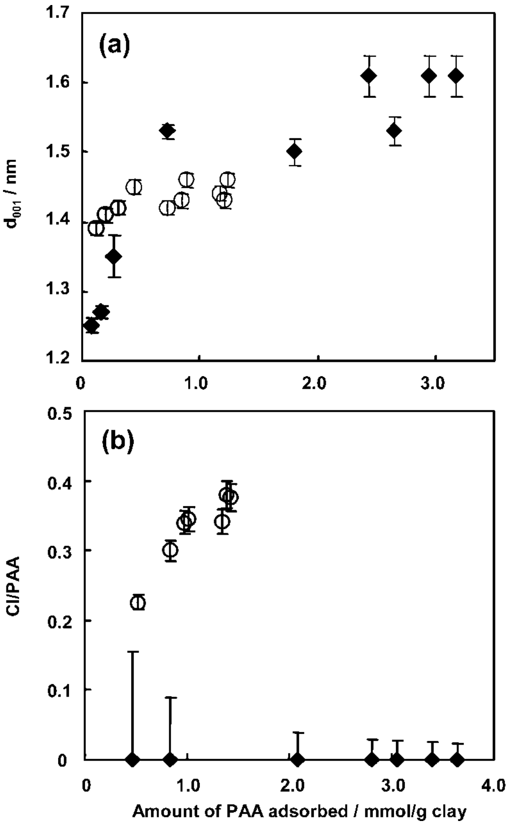

Figure 2. (a) *d* spacing of PAA/Na-TSM obtained at pH 3.0 (open circles) and 12.0 (solid diamonds) as function of the amount of PAA intercalated. (b) Molar ratio of Cl to PAA monomer units in PAA/Na-TSM prepared at pH 3.0 (open circles) and 12.0 (solid diamonds). Error bars on the solid symbols in part b correspond to the analytical detection limit of Cl (0.25%).

concentration of PAA (Figure 2), and the Cl/PAA ratio also increased from 0.2 to 0.4. These trends indicate that protonated PAA is squeezed into the interlayer galleries without significant vertical looping of the polymer chains. The molar ratio of adsorbed PAA to the CEC of Na-TSM (120 mequiv/100 g of clay) was estimated to be 1.17 in PAA/Na-TSM (5/1), consistent with partial charge compensation of NH_3^+ groups by intercalated Cl^- ions.

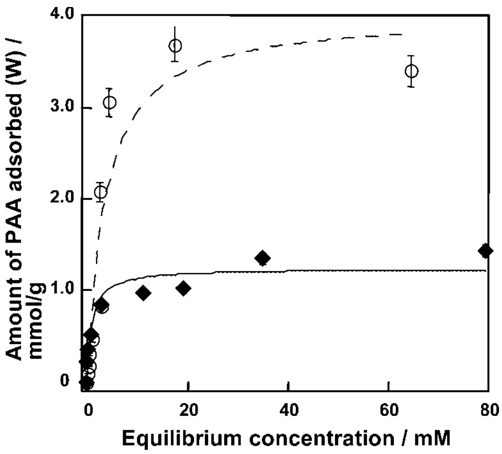

Figure 3. Adsorption isotherms of PAA on Na-TSM in aqueous dispersions at pH 3.0 (solid diamonds) and 12.0 (open circles) at 298 K. Lines show best fits to eq 1.

In contrast, for PAA intercalation at pH 12.0, where most of the primary amine groups are deprotonated,[18,20b,21,22] the basal spacing increases up to 1.6 nm as *n* is increased from 0.1/1 to 5/1 (Figure 1b). Almost twice as much PAA can be intercalated at pH 12.0, compared to pH 3.0, when excess PAA is used (Figure 2). The X-ray diffraction lines are broader for compounds made at pH 12.0, indicating a range of interlayer spacings and possibly a variety of PAA chain conformations within the galleries. The height of the intercalated gallery suggests a coiled conformation for intercalated PAA. In the FT-IR spectrum of PAA/Na-TSM (5/1) prepared at pH 12.0 (see the Supporting Information, Figure S1b), characteristic bands of the neutral primary amine group were observed at 1568(δ_s), 3377(υ_{as}), and 3277(υ_s) cm^{-1}, in addition to the scissoring vibration of protonated amine groups at 1633 cm^{-1}. This shows that some amine groups are ionized and can interact with the anionic clay surface, whereas others are neutral. PAA/Na-TSM made at high pH contains no Cl^-, within detection limits, and hence it is not expected to be an anion exchanger. However, it does have free amine groups with which to coordinate the surface of gold nanoparticles.

Free Energy of Intercalation of PAA into Na-TSM. Figure 3 shows adsorption isotherms at 298 K for PAA aqueous solutions at pH of 3.0–3.1 and 12.0–12.1 in equilibrium with PAA/Na-TSM. The amount of PAA intercalated and the equilibrium concentration of the polymer in the supernatant solution were calculated from an elemental analysis (C, H, and N) of the dried samples. On the basis of the Giles classification of solution adsorption isotherms,[23] both isotherms are H curves, as we previously observed for PDDA intercalation into Na-TSM.[14] The H curve is typical of polymer adsorption and indicates a high affinity between the host and guest. If the adsorption is Langmuirian (i.e., if the adsorbed or intercalated molecules interact weakly with each other, and there is a single adsorbed phase), then the

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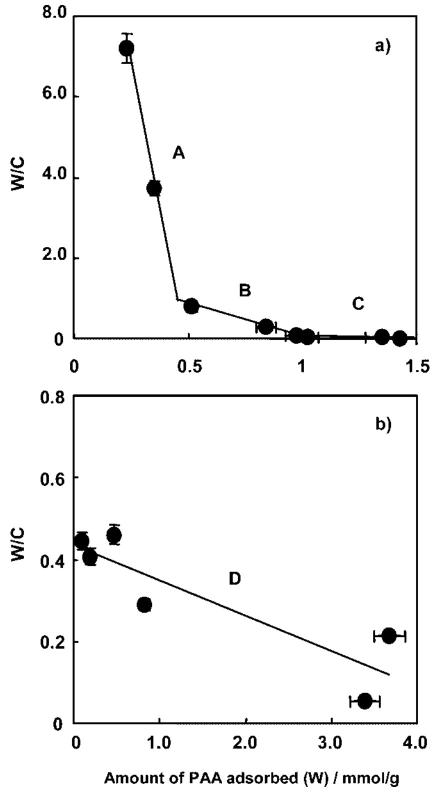

Figure 4. Scatchard plots derived from the data in Figure 3 for PAA/Na-TSM at pH 3.0 (a) and 12.0 (b). *W* is the amount of PAA intercalated into Na-TSM (mmol/g), and *C* is the equilibrium PAA concentration in solution. R^2 = 1.000, 0.9997, 0.8154, and 0.7856 for A, B, C, and D slopes, respectively.

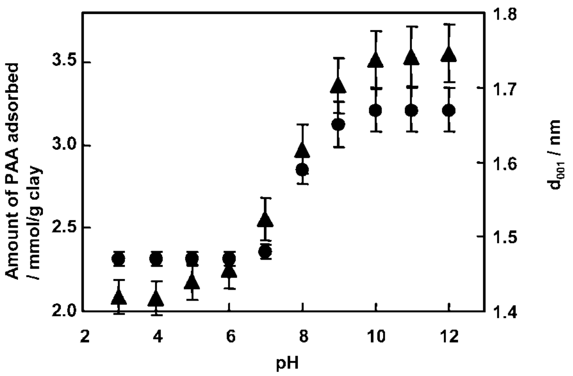

Figure 5. *d* spacing (solid circles) and adsorbed amount (solid triangles) of PAA as a function of the pH of the suspension during the washing process.

isotherm should follow eq 1, where *W* is the amount adsorbed, W_s is the saturation loading, and *a* is the equilibrium constant.[24]

$$W = aW_sC/(1 + aC) \qquad (1)$$

In order to determine the equilibrium constant (*a*) and the standard free energy ($\Delta G°_{ads}$)[26] of adsorption of PAA at high and low pH, the data in Figure 3 were replotted as Scatchard plots (Figure 4);[25,14a] in this form, the slope of the lines corresponds to –*a*. At low pH, the curve breaks into three linear regions, with changes in slope at approximately 0.45 and 1.0 mmol/g clay. From the slopes, $\Delta G°_{ads}$ values were estimated to be –64, –49, and –37 kJ mol^{-1}, at low, intermediate, and high loadings of PAA, respectively. While there is no obvious structural change (from the XRD patterns) that accompanies these changes in $\Delta G°_{ads}$, one can gain some insight into the intercalation equilibrium by considering the ratio of PAA to the CEC of the clay (1.2 meq/g). At the first break point in the curve, the charge on the clay is approximately half-compensated by the polymer, and like charges between NH_3^+ groups are well screened by intercalated water and some intercalated Cl^- ions. The second break point corresponds to ~60% charge compensation of the layer charge by NH_3^+ groups. Figure 2b shows that approximately 30% of the amine groups are charge-compensated by Cl^- at this point. At higher loading, intercalation becomes progressively less favorable because the anionic sheets are almost fully charge-compensated by NH_3^+ groups, and more Cl^- is needed to screen like charges between intercalated polycation chains.

In contrast, at high pH, although there is some scatter in the data, the entire isotherm can be described by a single equilibrium constant (*a* = 0.086 kmol^{-1} L), and the corresponding $\Delta G°_{ads}$ is –35 kJ mol^{-1}. The more positive value of $\Delta G°_{ads}$ at high pH is consistent with the free energy penalty of dissociating water to form the intercalation compound, as shown in reaction 2. At low pH, where the polymer is already in the protonated form, water dissociation is not needed for intercalation.

$$RNH_2(aq) + Na^+TSM^-(s) + H_2O(l) = RNH_3^+TSM^-(s) + Na^+(aq) + OH^-(aq) \qquad (2)$$

To draw an analogy again to the LbL assembly process, it has been reported that underlying negatively charged weak polyacid layers promote the protonation of weakly basic polymers when the latter are adsorbed at high pH.[21] In the PAA/Na-TSM system, the clay surface also has a negative charge, and that charge stabilizes the protonated amine groups associated with it, even at pH values well above the pK_a of the polymer in solution.

pH Effect on the Conformation PAA within the Interlayer Galleries. It has been reported that weakly basic polyelectrolytes on negatively charged surfaces have a higher pK_a or isoelectric pH relative to the same polymer in dilute aqueous solution.[20,21] To determine the effect of pH on the conformation of intercalated PAA, the intercalation compound (*n* = 5/1) prepared at pH 12.0 was washed with solutions of lower pH. Figure 5 shows the *d*-spacing and the amount of PAA remaining in the clay as a function of pH during the washing process. Between pH 12.0 and 10.0, the *d*-spacing and amount of adsorbed PAA were constant at 1.67 nm and 3.50 mmol/g of clay, respectively. Both the *d*-spacing and the loading decreased with decreasing pH between 10.0 and 6.0 and finally leveled off at 1.47 nm and 2.10 mmol/g of clay, respectively. ζ potentials of PAA/Na-TSM (5/1) suspensions at pH 3.0 to 13.0 are shown in Figure 6. From the ζ potential, the isoelectric point of PAA/Na-TSM (5/1) is

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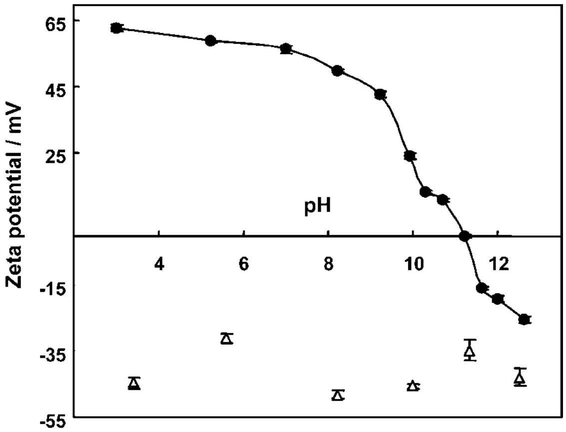

Figure 6. Acid–base equilibrium profile for PAA/Na-TSM (5/1) synthesized at pH 12.0 (solid circles) and for Au nanoparticles (open triangles).

about 11.0, indicating that most of free primary amine groups within the galleries are neutral above pH 11.0. The ζ potential increased below pH 10.0 and reached a plateau value of +60.0 mV at pH 7.0. The ζ potentials, *d*-spacings, and loading of PAA follow similar trends with pH, with the most significant changes occurring between pH 10.0 and 7.0. Protonation of the intercalated, largely neutral PAA chains causes them to dissociate from the clay, leaving behind an intercalation compound that is similar to that prepared directly at low pH. The sensitivity of the intercalated polymer chains to protonation is crucial in the intercalation of gold nanoparticles, which is described in the next section.

Intercalation of Gold Nanoparticles into PAA/Na-TSM. From XRD, infrared, and elemental analysis, it is apparent that PAA/Na-TSM prepared at pH 12 contains excess unprotonated amine groups in the interlayer. Therefore, PAA/Na-TSM (n = 5/1) obtained at pH 12 was used as a host for the intercalation of Au nanoparticles.

As we showed previously,[15] Au(S) nanoparticles are well-dispersed within the interlayer galleries of PAA/Na-TSM [see the Supporting Information for XRD patterns (Figure S2) and TEM images (Figure S3) of intercalation compounds containing Au(S)]. The average diameters of nanoparticles in Au(S)/PAA/Na-TSM (0.079–1.27) and before intercalation are compared in Table 1. The diameter showed a slight tendency to increase with increasing Au loading and reached 2.1 ± 0.5 nm at the saturation loading (1.27). By comparison to the diameter of Au(S) before intercalation, 1.6 ± 0.3 nm, it can be concluded that very little aggregation or coalescence due to Ostwald ripening[27] occurs. From nitrogen adsorption isotherms, the Brunauer–Emmett–Teller (BET) surface area of Au(S)/PAA/Na-TSM (0.79) was 25.7 m^2/g. Considering that the BET surface area of PAA/Na-TSM (5/1) is 18.6 m^2/g, the surface area did not substantially increase after Au(S) intercalation. This indicates that Au(S)/PAA/Na-TSM does not have a porous structure as do well-known pillared clay materials. By comparing the intercalations of Au(S), Au(L), and Au(XL) into PAA/Na-TSM (n = 5/1), there appears to be a limit of about 5 nm for particle intercalation (see the Supporting Information, Figure S4). This size exclusion may reflect a limit of the flexibility of the intercalated PAA chains, which must extend across the gallery in "accordion" fashion when large nanoparticles are intercalated.

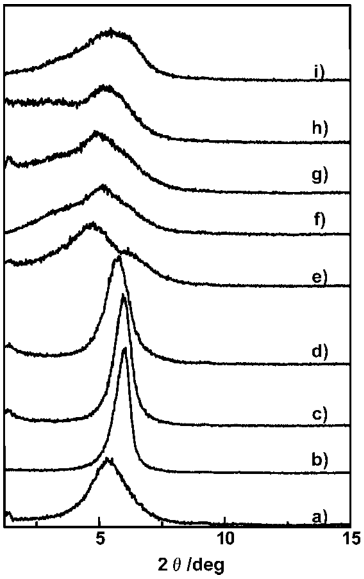

Figure 7. XRD patterns of PAA/Na-TSM and Au(S)/PAA/Na-TSM obtained under different pH conditions: PAA/Na-TSM (5/1) prepared at pH 12.0 (a) and Au(S)/PAA/Na-TSM obtained by intercalating Au(S) at pH (b) 3.0, (c) 6.0, (d) 7.0, (e) 8.0, (f) 9.0, (g) 10.0, (h) 11.0, and (i) 12.0.

pH Effect on Au Nanoparticle Intercalation into PAA/Na-TSM. We have already reported that Au–primary amine covalent bonding is the key interaction for the stable intercalation of Au nanoparticles into PAA/layered oxides.[15] As noted above, the state of protonation of the primary amine groups on PAA in the interlayer, and the overall charge on the intercalated clay, can be controlled by changing the pH. Because both can influence the intercalation of anionic nanoparticles, we studied the effect of pH on the nanoparticles' intercalation reaction. Figure 7 and Table 2 show, respectively, XRD patterns and the amounts of Au(S) intercalated at different pH values (3.0–12.0). At low pH (3.0–7.0), there was negligible incorporation of anionic Au(S) into PAA/Na-TSM. Despite the presence of some exchangeable Cl^- in the galleries under these conditions, the strong electrostatic interactions between protonated PAA and the enclosing anionic clay sheets do not allow the galleries to expand to accommodate the anionic Au nanoparticles. TEM images (Figure 8) show that under these conditions a small amount of Au(S) is adsorbed on the outer surface of the composites. At pH > 8.0, neutral amine groups are available to coordinate the Au(S) particles, and the loading increases. TEM images (Figure 8c–e) show, however, that Au nanoparticles aggregate on the PAA/Na-TSM outer surface at pH 8.0–10.0. Because some intercalated PAA chains (in the material synthesized at pH 12.0) are eliminated from the galleries at lower pH (Figure 5), the excess PAA can promote nanoparticle aggregation on the outer surface of the clay. At pH 11.0, intercalated Au nanoparticles are well-dispersed within the interlayer (Figure 8b), and a prominent broad shoulder is observed on the low-angle side of the PAA/Na-

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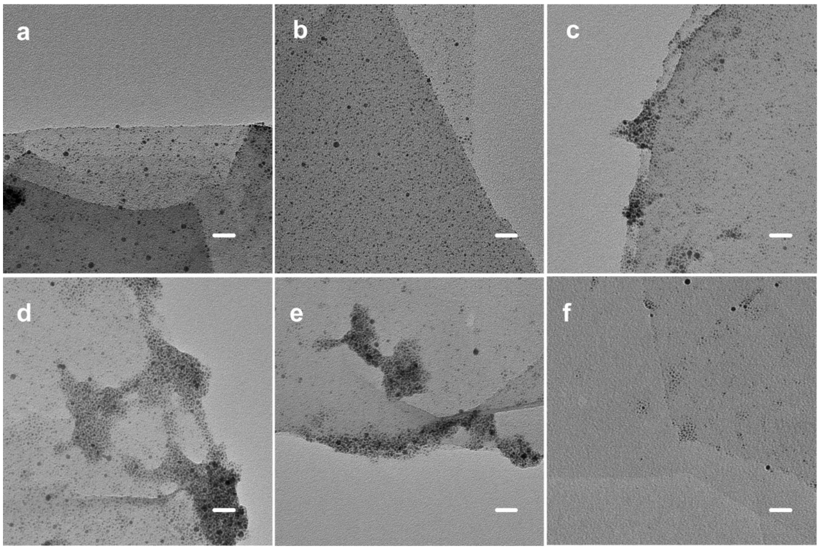

Figure 8. Typical TEM images of Au(S)/PAA/Na-TSM obtained under different pH conditions: (a) 12.0, (b) 11.0, (c) 10.0, (d) 9.0, (e) 8.0, and (f) 7.0. The scale bar is 20 nm.

Table 1. Average Diameter of Intercalated Au Nanoparticles

loading of Au(S) into PAA/Na-TSM /mmol/1g clay	0.079	0.40	0.79	1.27
average diameter of Au(S) accommodated /nm	1.60 ± 0.22	1.72 ± 0.33	1.70 ± 0.60	2.10 ± 0.46

Table 2. Amounts of Au(S) Adsorbed and/or Intercalated into PAA/Na-TSM Different pH Conditions

pH of the reaction suspention	3.0–3.1	6.0–6.1	7.0–7.1	8.0–8.1	9.0–9.1	10.0–10.1	11.0–11.1	12.0–12.1
adsorbed amount of Au(S) /mmol/ 1g of Na-TSM	0.00	0.00	0.04	0.40	0.40	0.40	0.40	0.35

TSM peak in the corresponding XRD pattern. As the pH is increased to 12.0, the Au loading decreased slightly, and some aggregation of the nanoparticles was observed. Referring back to Figure 6, one can see that under this condition the Au(S) and PAA/Na-TSM particles are both negatively charged. Electrostatic repulsion between the colloidal particles may inhibit the reaction of Au nanoparticles with PAA/Na-TSM. This interpretation is also supported by the observation that, when the reaction time is increased from 2 to 18 h at pH 12.0, the amount of Au(S) intercalated is the same as that found at pH 11.0. This series of experiments shows that both the covalent interaction between neutral amine groups and Au(s) and the electrostatic interactions between colloidal particles are important in controlling the intercalation of Au(S). Both interactions are optimized at pH 11.0, which is where we observe the highest loading and most uniform dispersion of intercalated Au(S) nanoparticles in PAA/Na-TSM.

Optical Absorbance of Au/PAA/Na-TSM Composites. In order to evaluate the spectroscopic properties of Au/PAA/Na-TSM, Au(L) was used as a guest nanoparticle because of its strong plasmon resonance relative to Au(S). XRD patterns and TEM images of Au(L)/PAA/Na-TSM (Figures S5 and S6, Supporting Information) show that Au(L) nanoparticles are well-dispersed within the interlayer at pH 11.0. Figure 9 shows UV–vis absorption spectra of Au(L) nanoparticles and of 0.0625 wt % Au(L)/PAA/Na-TSM (0.40 and 0.79) suspensions in water. In water, the plasmon resonance maximum of Au(L) was observed around 510 nm. For the intercalated nanoparticles, regardless of the loading, the absorption peak was broadened and the maximum slightly red-shifted (to ca. 525 nm). Cho and Caruso have found that the plasmon resonance band broadens and shifts slightly to the red when Au nanoparticles are dispersed in aqueous PAA solutions, consistent with our observations.[22] The broadening and red-shift can be attributed to a reduced nanoparticle–nanoparticle distance[28] and to a change in the refractive index of the medium.[29]

Diffuse reflectance spectra of Au(L)/PAA/Na-TSM powders with different Au loadings are shown in Figure 10. At relatively low loading (0.040 and 0.079), a broad absorption band with $\lambda_{\max} = 535$ nm is observed. At higher loading (0.40 and 0.79), a shoulder extending from 570 to 730 nm was observed on the band at 535 nm. We tentatively interpret this new spectral feature as arising from close contacts between Au(L) nanoparticles in the galleries. It was known from several modeling studies that plasmonic hybridization between adjacent metallic nanoparticles occurs when the interparticle distance is less than 10 nm.[30] Wang et al. recently reported the fabrication of

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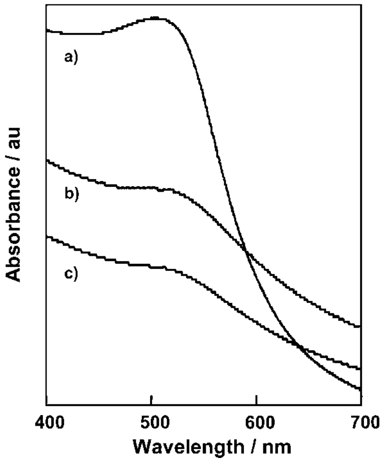

Figure 9. UV–vis absorption spectra of Au(L) suspension (a), and 0.0625 wt % aqueous suspension of Au(L)/PAA/Na-TSM (0.79) (b) and (0.40) (c).

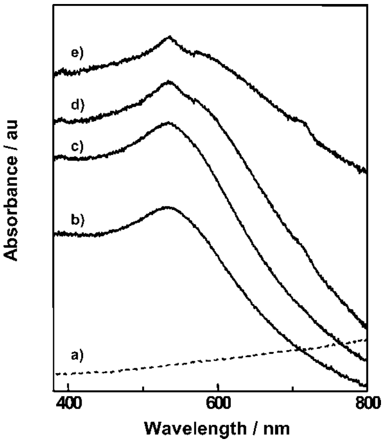

Figure 10. Diffuse reflectance spectra of PAA/Na-TSM (a) and Au(L)/PAA/Na-TSM (0.040) (b), (0.079) (c), (0.40) (d), and (0.79) (e).

well-ordered Au nanosphere (50-nm diameter) arrays with spacings of less than 8 nm between adjacent nanoparticles and their unique optical properties for surface-enhanced Raman scattering.[31] In their work, isolated Au nanopartricles showed an absorption band in the visible region; in contrast, the arrays had a broad plasmon resonance from the visible to the near-infrared, which arose from a coalescence of the dimer plasmon resonances of individual junctions. With an increase of the Au loading in Au(L)/PAA/Na-TSM, the horizontal interparticle distance within the interlayer decreases; in addition, the vertical interparticle distance through the silicate sheets also decreases and in the limit becomes comparable to d_{001} spacing in the XRD pattern of the dried composite. For Au(L)/PAA/Na-TSM in aqueous suspensions, the degree of layer stacking is relatively small, so only the in-plane interaction between nanoparticles is effective.

Conclusions

The intercalation of a basic polyelectrolyte, PAA, into a synthetic Na-fluoromica is markedly different under conditions of low (3.0) and high (12.0) pH. In the former case, the saturation loading was lower but the free energy of intercalation was more favorable. At low pH, the PAA polymer chains are completely protonated, and at high loadings, chloride ions are also intercalated to screen the repulsive interactions between adjacent polycation chains. Although the low-pH PAA/Na-TSM compounds have some ion exchange capacity, they do not intercalate anionic Au nanoparticles, most likely because of the energetic penalty of expanding the interlayer. PAA/Na-TSM compounds made at high pH have a higher saturation loading of PAA, although the intercalation is less favorable thermodynamically. Under these conditions, the layer charge is entirely compensated by protonated primary amine groups, and there is no intercalated Cl^-. While these materials are not anion exchangers, they are able to bind anionic Au nanoparticles through covalent interactions with free amine groups in the galleries. The optimum pH for intercalation of Au nanoparticles is at 11.0, where the PAA/Na-TSM has relatively little charge; the metal colloids are negatively charged, and there is a sufficient loading of neutral amine groups in the galleries to bind the nanoparticles.

In spectroscopic measurements of Au nanoparticles intercalated into PAA/Na-TSM, the red-shift in the plasmon resonance of Au nanoparticles can be attributed to a change of dielectric properties of the medium, relative to aqueous solutions, and weak interactions between particles within each interlayer gallery. At a high loading of Au nanoparticles, some unusual features in the plasmon resonance spectrum were observed in the long-wavelength region (570–730 nm), which may arise from interlayer particle interactions. This convenient route to well-dispersed noble metal nanoparticles intercalated into layered materials thus offers some potential for new optical applications based on plasmon resonance.

Finally, in terms of the catalytic applications of intercalated gold nanocrystals, we carried out some prelimary experiments designed to remove PAA from Au/PAA/Na-TSM composites through calcination, room-temperature chemical oxidation, and photo-oxidation. To burn out PAA confined within the interlayer, relatively high temperatures were needed, as confirmed by TGA-MS experiments in which carbon dioxide and H_2O derived from PAA combustion were observed from 220 to 780 °C. Under these conditions, Au nanoparticles are largely eliminated from the galleries and coalesce to form larger particles. In a piranha (3:7 30% H_2O_2/conc. H_2SO_4) solution, Au nanoparticle coalescence occurred along with the degradation of PAA chains; under these acidic conditions, however, one should not expect to retain nanoparticles coordinated by neutral amine groups in the galleries. Preliminary unsuccessful attempts were also made to oxidize PAA photocatalytically within the galleries of the lamellar semiconductor $HCa_2Nb_3O_{10}$. Therefore, the dispersion of polymer-free Au nanoparticles for catalytic applications within the galleries remains a challenge.

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Supporting Information Available: FT-IR spectra of PAA/Na-TSMs obtained at high and low pH, XRD patterns of PAA/Na-TSM (5/1) and Au(S)/PAA/Na-TSM with different Au loadings, TEM images of Au(S) and Au(S)/PAA/Na-TSM with different Au loadings as well as Au(XL)/PAA/Na-TSM (0.40), XRD patterns of Au(L)/PAA/Na-TSM with different Au loadings, and TEM images of Au(L)/PAA/Na-TSM with different Au loadings. This material is available free of charge via the Internet at http://pubs.acs.org.

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