Buildup of Polymer/Au Nanoparticle Multilayer Thin Films Based on Hydrogen Bonding

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We report two new hydrogen-bonding-based routes for layer-by-layer fabrication of polymer/Au nanoparticle multilayer thin films. Two types of Au nanoparticles surface-modified with carboxyl groups or pyridine groups were prepared in nonaqueous solvents. In the first assembly route, we consecutively adsorbed poly(4-vinylpyridine) (PVP) and Au nanoparticles with carboxyl group tailored surfaces. In the second route, we alternatively deposited poly(acrylic acid) (PAA) and Au nanoparticles with pyridine group tailored surfaces. The multilayer buildup was monitored by UV−vis spectroscopy, which showed a linear increase of the film absorbance with the number of adsorbed Au layers. FTIR spectroscopy was used to verify hydrogen bonding between the pyridine and carboxyl groups, which is believed to be the driving force for the formation of polymer/Au multilayer thin films.

Introduction

Metallic and semiconductor nanoparticles represent an advanced materials dimension that bridges bulk material and molecular behavior and offers prospects of novel and even size-dependent chemical, electronic, and physical properties.[1,2] Extensive studies have been carried out to organize nanoparticles into thin films, mainly by Langmuir−Blodgett (LB) techniques and self-assembly methods.[3−5] Recently, a well-established layer-by-layer (LBL) assembly method, initially developed for pairs of oppositely charged polyelectroytes,[6] has been successfully applied to the preparation of thin films of nanoparticles from aqueous solutions. The fabrication of LBL films is based on electrostatic interactions between sequentially adsorbed monolayers of nanoparticles and oppositely charged polyelectrolytes. Many nanoparticles, such as TiO_2, CdSe, and Au, were assembled successfully into thin films, for which a number of advanced electronic and photonic applications have been demonstrated.[7−10] There remains great interest in fabricating thin films in the nanometer range with vertical organization of different sandwich-like layers based on new strategies. For example, the fabrication of organic/inorganic hybrid multilayer films based on metal−ligand coordination has been reported.[11,12]

Recently, two new hydrogen-bonding-based approaches to fabrication of alternating multilayer polymer films were developed by Rubner et al.[13] using polyaniline and by Zhang et al.[14] using poly(vinylpyridine)/poly(acrylic acid) (PVP/PAA). These works confirmed that relatively strong secondary forces could be used to assemble multilayer thin films in a layer-by-layer manner. In this paper, we report the layer-by-layer assemblies of polymer/Au nanoparticles based on hydrogen-bonding interactions. Au nanoparticles surface-modified with carboxyl groups or pyridine groups were prepared in nonaqueous solvents. Surface-modified Au nanoparticles and polymers, having suitable hydrogen-bonding complementary partners, were then used to fabricate hybrid organic/inorganic mulitlayer films in a layer-by-layer manner.

Experimental Section

Materials. Poly(4-vinylpyridine) (PVP) (M_w 6.0 × 10^4), poly(acrylic acid) (PAA) (M_w 2.4 × 10^5), polyethylenimine (PEI) (M_w 7.5 × 10^5), 4-mercaptobenzoic acid (4-MBA), hydrogen tetrachloroaurate (III) trihydrate, and sodium borohydride were purchased from Aldrich. Methanol and acetic acid were used as available.

Preparation of Au Nanoparticles with Carboxyl Group Tailored Surfaces (4-MBA-Au). Au nanoparticles stabilized by 4-mercaptobenzoic acid (4-MBA, $HS-C_6H_4-COOH$) were synthesized in methanol/acetic acid solution using a modified procedure published by Brust and co-workers.[15] Briefly, 0.40 mmol of tetrachloroauric acid and 1.2 mmol of 4-mercaptobenzoic acid were co-dissolved in 35 mL of 6:1 methanol/acetic acid, producing a yellow solution. $NaBH_4$ (0.3 g, 8 mmol) in 15 mL of methanol was added with rapid stirring. The solution immediately changed to a black suspension and began to

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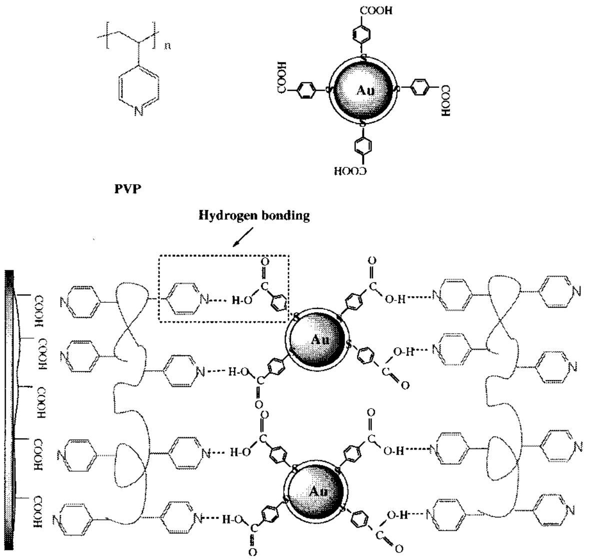

Figure 1. Schematic representation of the buildup of multilayer assembly by consecutive adsorption of PVP and 4-MBA-Au nanoparticles.

reflux. The suspension was stirred for an additional 30 min after it returned to room temperature. The solvent was then removed under vacuum. The black product was washed several times with diethyl ether and dried under a stream of N_2. The sample was soluble in water and other polar solvents such as methanol.

Preparation of Au Nanoparticles with Pyridine Group Tailored Surfaces (Py-Au). Briefly, 55.8 mg of PVP was dissolved in 150 mL of methanol. 70.8 mg of $HAuCl_4$ in 10 mL of methanol was added under rapid stirring. The molar ratio of metal salts to pyridine units was about 1:2. Ten minutes later, 27 mg of $NaBH_4$ in 10 mL of methanol was added quickly. A change of color from yellow to pink was immediately observed, indicating the formation of Au nanoparticles. In addition, the pH of the solution increased because of homogeneous reduction. The temperature of the Au colloid returned to room temperature after 30 min of further stirring.

Fabrication of Polymer/Au Nanoparticle Multilayer Film. To fabricate LBL films of polymer/Au nanoparticles, it was first necessary to pretreat the substrates. The first step was to modify the substrates (e.g., quartz, CaF_2 plates, and carbon-coated copper grids) to create an NH_2-tailored surface by immersing them into a branched polymer (PEI) (0.5 wt %) solution. PEI is an attractive choice because it can adhere to a variety of substrate surfaces.[9] Au nanoparticles with carboxyl group and pyridine group tailored surfaces were assembled according to the following two routes.

(I) Layer-by-Layer Assembly of PVP and 4-MBA-Au Nanoparticles. The PEI-pretreated substrates were transferred to a PAA (0.252 g/L) methanol solution for 10 min, resulting in a COOH-tailored surface. The substrates were then immersed in a PVP (0.256 g/L) methanol solution for 5 min to add a layer of PVP. After rinsing with methanol, the substrates were then transferred to a methanol/acetic acid (10:1) solution of Au nanoparticles for 10 min, adding one layer of Au nanoparticles. Multilayer films can be obtained by repeating the last two steps, as shown schematically in Figure 1.

(II) Layer-by-Layer Assembly of PAA and Py-Au Nanoparticles. As schematically shown in Figure 2, the synthesis of Au nanoparticles in the presence of PVP resulted in pyridine group tailored surfaces, allowing alternating deposition with PAA based on the hydrogen-bonding interactions between pyridine groups on the surface of Au nanoparticles and carboxyl groups of PAA. Briefly, the PEI-pretreated substrates were first immersed in a PAA (0.252 g/L) methanol solution for 10 min, resulting in a COOH-tailored surface. After washing with methanol, the substrates were transferred to a methanol solution of PVP-capped Au nanoparticles for another 10 min, adding one layer of Au nanoparticles. Multilayer films can be obtained by repeating the last two steps.

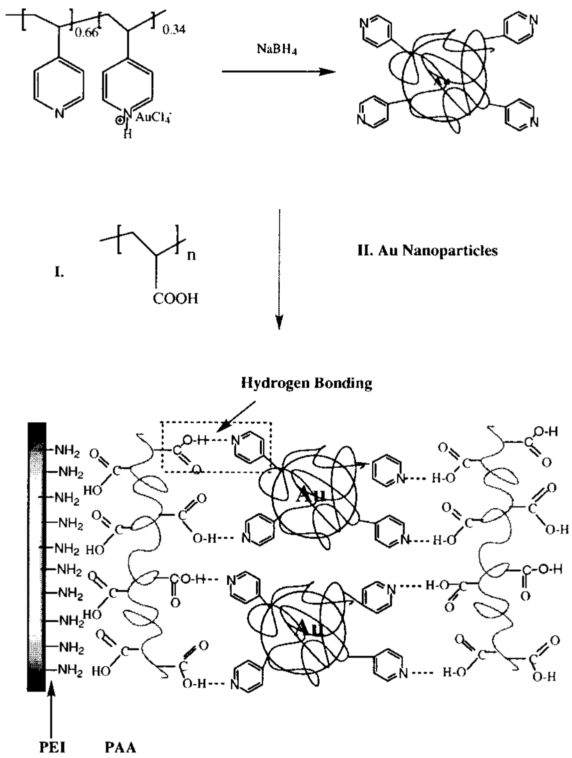

Figure 2. Schematic representation of the synthesis of Py-Au nanoparticles and the buildup of multilayer assembly by consecutive adsorption of PAA and Py-Au nanoparticles.

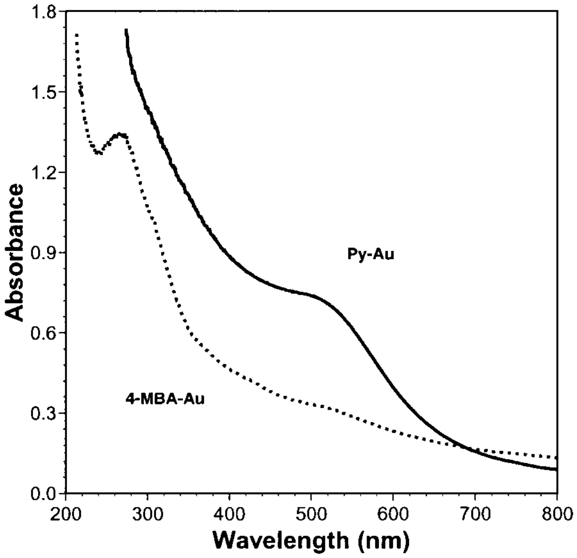

Figure 3. UV−vis spectra of 4-MBA-capped Au nanoparticles and Py-Au nanoparticles in methanol.

Results and Discussion

Au Nanoparticles. The UV−vis spectrum of 4-MBA-capped Au nanoparticles in methanol solution (Figure 3, bottom curve) showed only a weak surface plasmon (SP) band, which was similar to other alkanethiolate-protected Au nanoclusters.[16,17] The Au nanoparticles were all round in shape and had an average diameter of about 2.6 ± 0.9 nm, measured by transmission electron microscopy (TEM).

PVP is known to be a strong metal-chelating agent.[18,19] For example, polystyrene-*b*-poly(4-vinylpyridine) copoly-

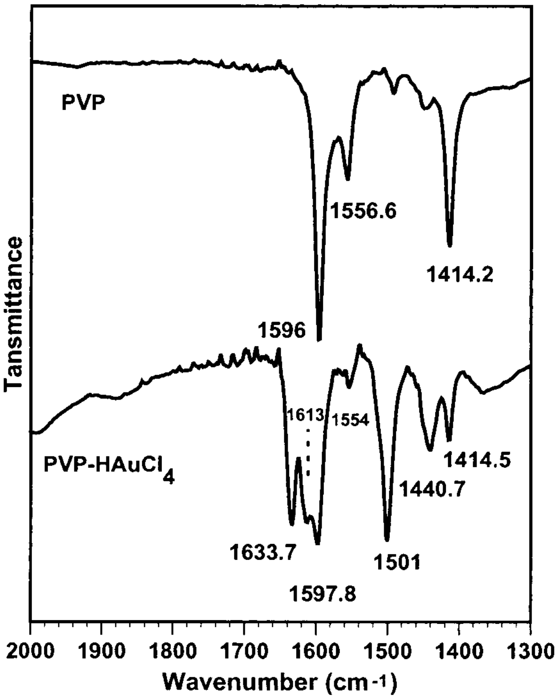

Figure 4. Comparison of the IR spectra of pure PVP and PVP with $HAuCl_4$.

mers can be used to synthesize Au nanoparticles.[18,19] Here, we were able to synthesize Au nanoparticles in the presence of pure PVP, producing pyridine group tailored surfaces (hydrogen-bonding acceptors). The binding of $HAuCl_4$ to pyridine groups of PVP was followed by FTIR spectroscopy. The comparison of the spectra of PVP with and without $HAuCl_4$ ($HAuCl_4$/pyridine units, 1:2) is shown in Figure 4. The decreasing intensity of bands characteristic of the pyridine units (1557 and 1414 cm^{-1}) and the appearance of new bands (1634, 1613, and 1501 cm^{-1}) were attributed to the protonation of the pyridine units.[19] The UV−vis spectrum of Py-Au methanol solution (Figure 3, upper curve) showed a pronounced SP band around 530 nm. The resulting solution was very stable. Its UV−vis spectrum did not show any sign of particle aggregation over a half-month at room temperature.

Layer-by-Layer Assembly. Multilayer film buildup was monitored using UV−vis spectroscopy. No polymer absorption was found in the visible region. When Au nanoparticles were adsorbed onto the film, an absorption in the visible region emerged. Figure 5 shows the UV−vis absorption spectra of the multilayer film of PVP/(4-MBA-Au) with different number of bilayers on a quartz slide. The absorption spectra of PVP/(4-MBA-Au) nanoparticle multilayer films were in agreement with that of the Au nanoparticle solution, illustrating a successful assembling of 4-MBA-Au nanoparticles into the film. In addition, a linear increase of the absorbance with the number of bilayers (inset of Figure 5) was observed, indicating that approximately the same amount of Au nanoparticles were adsorbed in every deposition cycle.

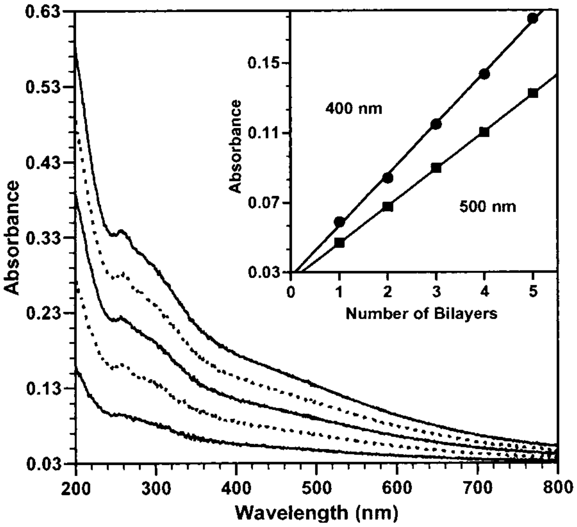

Figure 5. UV−vis absorption spectra of the PVP/(4-MBA-Au) nanoparticle multilayer films with different numbers of bilayers. From the lower to upper curves, the number of PVP/(4-MBA-Au) bilayers is 1, 2, 3, 4, and 5. Shown in the inset is a plot of the absorbance at 400 and 500 nm vs the number of PVP/(4-MBA-Au) bilayers.

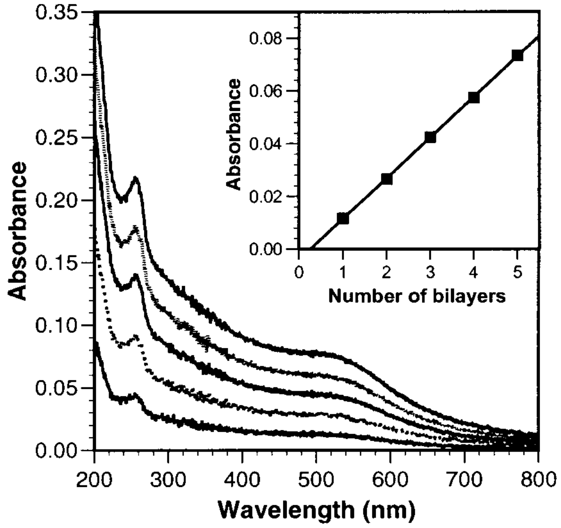

Figure 6. UV−vis absorption spectra of PAA/(Py-Au) nanoparticle multilayer thin films with different numbers of bilayers. From the lower to upper curves, the number of PAA/(Py-Au) bilayers is 1, 2, 3, 4, and 5. The inset is a plot of the absorbance at 530 nm vs the number of PAA/(Py-Au) bilayers.

For the PAA/(Py-Au) LBL film, similar results (Figure 6) were observed, indicating again a stepwise and uniform assembly process. Such behavior was observed in many layer-by-layer deposition systems based on electrostatic interaction.[7−10] Therefore, the hydrogen-bonding-based assembly provided an alternative way to fabricate homogeneous organic/inorganic multilayer films in a layer-by-layer manner.

The PVP/(4-MBA-Au) LBL film was also studied by small-angle X-ray diffraction (SAXD), which is a convenient and direct method for the determination of film thickness.[20,21] Figure 7 shows the SAXD pattern of a

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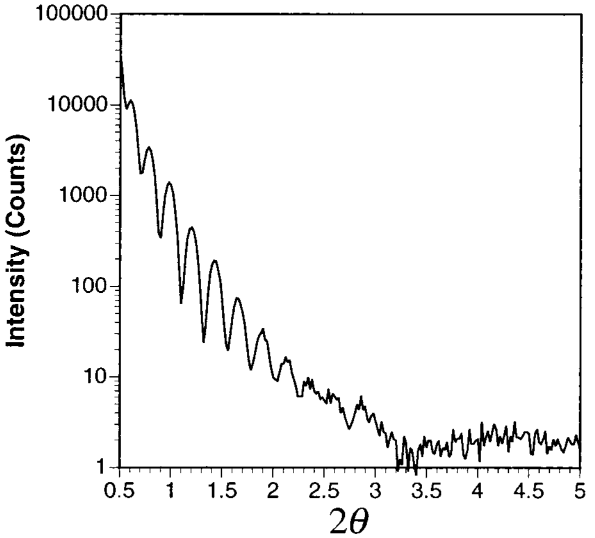

Figure 7. Small-angle X-ray diffraction pattern of a 12-bilayer film of PVP/(4-MBA-Au) on a quartz substrate.

12-bilayer film of PVP/(4-MBA-Au) on a quartz substrate. The X-ray curve revealed well-defined Kiessig fringes, which indicated that the PVP/(4-MBA-Au) LBL film was uniform and flat. The total thickness of the film was estimated to be about 39.6 nm from the oscillation period. Since the UV−vis results demonstrated a stepwise and uniform assembly process, the thickness of one PVP/Au bilayer was calculated to be about 3.3 nm. This is consistent with the average size of 2.6 nm for the 4-MBA-Au particles.

The direct evidence for hydrogen bonding between poly(4-vinylpyridine) and 4-MBA on the surface of Au nanoparticles was obtained using FTIR spectroscopy. Hydrogen bonding between pyridine groups and carboxyl groups resulted in a splitting pattern of the OH stretching bands.[22,23] Figure 8 shows the IR spectra of a cast film of 4-MBA-Au nanoparticles, a cast film of PVP, and a 10-bilayer PVP/(4-MBA-Au) film on CaF_2 plates. The spectrum of the 4-MBA-Au nanoparticles shows a pronounced C=O band at 1678 cm^{-1}, which is consistent with that of 4-MBA in KBr glass.[24] This band, as well as the broad OH stretch (~3450 cm^{-1}), indicates hydrogen-bonding interaction between terminal carboxyl groups of 4-MBA on the surface of Au nanoparticles.[16b,24] The spectrum shows no C=O stretching band of the monomeric form of carboxylic acid groups, which was observed at 1749 cm^{-1} for self-assembled monolayers of 4-MBA on Au film[24] and at 1724 cm^{-1} for 4-MBA modified Au nanoparticles.[16b] Instead, there was an excess of thiol molecules, as indicated by the S−H stretch bands at ca. 2555 cm^{-1}. We believe that these excess thiol molecules formed H-bonds with the terminal carboxylic acid groups of Au nanoparticles, resulting in the absence of the monomeric form of the C=O stretch in the spectrum. Also shown in the spectrum is the ring vibration of 4-MBA at 1589 cm^{-1}.[24] The absorption peaks at 1595.8, 1556.6, and 1414.2 cm^{-1} in the spectrum of the cast film of PVP are assigned to ring vibrations of pyridine groups of PVP.[14]

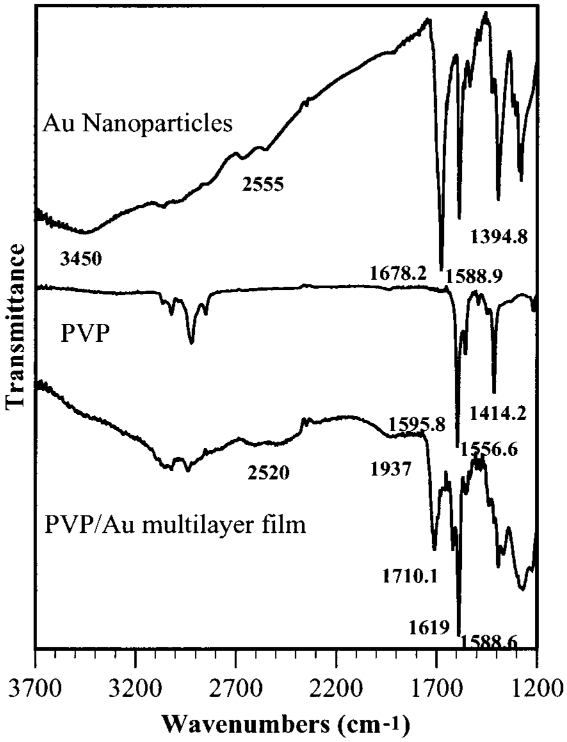

Figure 8. FTIR spectra of a cast film of PVP, a cast film of 4-MBA-Au nanoparticles, and a 10-bilayer PVP/(4-MBA-Au) film on CaF_2 plates.

After Au nanoparticles were assembled into multilayer film, the C=O stretching vibration was shifted to 1710 cm^{-1}. This indicated hydrogen bonding between the acid hydroxyl groups and pyridine groups. Another striking feature is the appearance of new bands at 1937 and 2520 cm^{-1}. These bands were assigned to the stretching bands of hydrogen-bonded OH groups based on a similar splitting pattern of OH groups observed in polymer blends containing carboxyl groups and vinylpyridine groups.[22,23] The presence of these bands in the multilayer thin films indicated strong hydrogen bonding between the carboxyl groups (donors) on the surface of Au nanoparticles and pyridine groups (acceptors) of PVP. The peaks in the spectral region from 1650 to 1400 cm^{-1} were difficult to assign because of overlapping absorption, although they arise mainly from the ring vibration of both 4-MBA and pyridine groups.

Figure 9 shows the FTIR spectra of a cast film of PAA and a 10-bilayer PAA/(Py-Au) film on CaF_2 slides. The IR spectrum of pure PAA shows a broad absorption band around 3000 cm^{-1} and the C=O stretching vibration at 1709 cm^{-1}, indicating that the polymer was in an associated state.[14] For the PAA/(Py-Au) LBL film, the C=O stretching vibration appeared at 1723 cm^{-1}, indicating the carboxyl groups were in a less associated state than that in pure PAA. Moreover, O−H stretching vibrations appeared at 2530 and 1943 cm^{-1}, indicating strong hydrogen bonding between the carboxyl groups of PAA and pyridine groups on the surface of Au nanoparticles.[22,23] Ring vibrations of pyridine groups at 1605, 1557, and 1416 cm^{-1} were also observed. These

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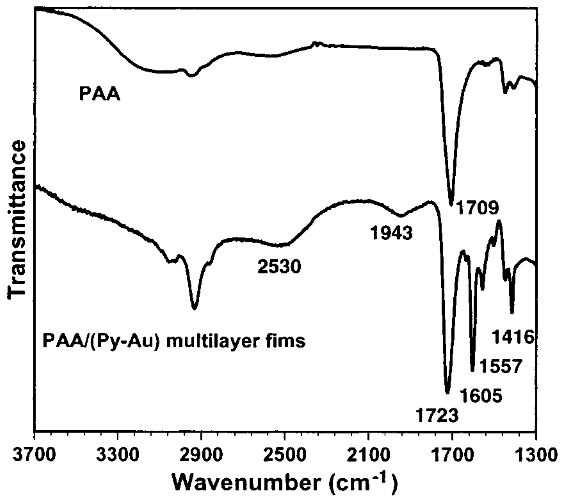

Figure 9. FTIR spectra of a cast film of pure PAA and a 10-bilayer PVP/(Py-Au) film on CaF_2 plates.

results indicate that strong hydrogen bonding was present in the PAA/(Py-Au) multilayer film.

Conclusion

We have developed two approaches for the layer-by-layer assembly of polymer/Au nanoparticles multilayer films based on hydrogen bonding. The multilayer buildup was monitored by UV−vis spectra, which showed a linear increase of the film absorbance with the number of adsorbed Au layers. The resulting films had a high degree of flatness and smoothness as indicated by SAXD. Hydrogen-bonding interaction between the pyridine groups of PVP and the carboxyl groups was verified by FTIR spectroscopy and is believed to be the driving force for the formation of PVP/Au multilayer thin films. Our preliminary work indicates that a similar strategy can be employed for assembling other surface-modified semiconductor and metal nanoparticles (such as CdS, CdSe,[25] and Ag) into thin films. We believe that the reported method can be used as an alternative way for the construction of polymer/nanoparticles LBL films.

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