Fabrication of Polymer/Inorganic Nanoparticles Composite Films Based on Coordinative Bonds

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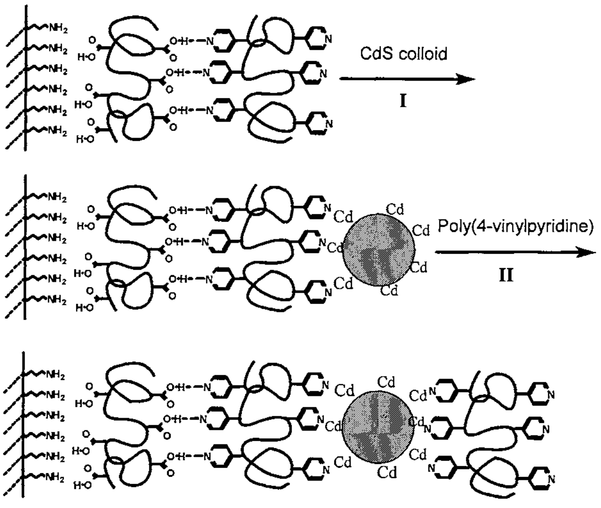
We reported a new approach for fabrication of a multilayer film through coordinate bonds of pyridine polymers and CdS nanoparticles, which was identified by UV-Vis and FTIR spectroscopy.

The organization of nano-sized particles into layered structures, mainly by Langmuir-Blodgett technique and self-assembly methods, has various potential applications in advanced optical and electronic devices.[1,2] The driving forces for self-assembly and LB particulate films are strong ionic (or coordinative) bonds and weak van der Waals interaction, respectively.[1] Since Decher et al.[3] demonstrated the application of ionic attraction to construct multilayer polymer films, the assembly technique has been extended to other materials such as colloids and proteins.[1,2,4,5] However, self-assembly films based on coordination or covalent chemistry were restricted to certain classes of organics.[2]

As it is well known, the typical coordination complexation between pyridine and some transition metals has been studied.[6] Polymers containing coordinated metal salts have been used to prepare inorganic nanoparticle/polymer hybrid materials.[7,8] In these systems, the polymer not only acts as the encapsulant for the particles, but also confers the stability by bonding to surface metal atoms via coordinative bonds to terminate the particle growth.[7] Recently, a kind of self-organizing film of PVP/PSS($Cu_{1/2}$) was fabricated based on coordinative bonds and then successfully constructed heterostructured film via in-situ chemical reaction in a restricted area.[9] Here, we reported another approach for fabrication of a polymer/inorganic nanoparticles multilayer film by directly alternating deposition poly(4-vinylpyridine) and CdS nanoparticles with general Cd-rich surfaces based on coordinative bonds.

Colloidal CdS nanoparticles in N,N-dimethylformamide (DMF) were prepared according to the reference.[10] Less than the stoichiometric amount H_2S gas was introduced into a N_2-purged DMF solution (40 mL) of a cadmium salt (5 mM) with vigorous stirring on an ice bath. The colloidal CdS nanoparticles were stabilized by solvation of the oxygen atoms of DMF to the cadmium atoms on the surface of CdS.[10] Poly(4-vinylpyridine) (PVP) was prepared by polymerization of 4-vinylpridine in methanol with 2,2'-azoisobutyronitrile (AIBN) at 56 °C for 20 h.[11] Molecular weight $\overline{Mw}$ is about 1×10^5 measured by GPC method.

The construction of the CdS/PVP multilayer film is simply shown in Scheme 1 and described as follows: the first step was to modify the corresponding substrate to create surface covered with pyridine groups according to the literature.[12] The resulting substrate was then dipped into a colloidal CdS solution for 30 min to adsorb one layer of CdS nanoparticles. After washed with DMF and methanol, the substrate was transferred to the PVP methanolic solution (0.26 g/L) for 30 min, thus adsorbing a PVP layer. After rinsed with methanol, the substrate was again dipped into colloidal CdS solution for 30 min to get another CdS layer. The CdS/PVP multilayer films were prepared through repeating the



Scheme 1. Schematic drawing for the build-up of alternating film of PVP/CdS.

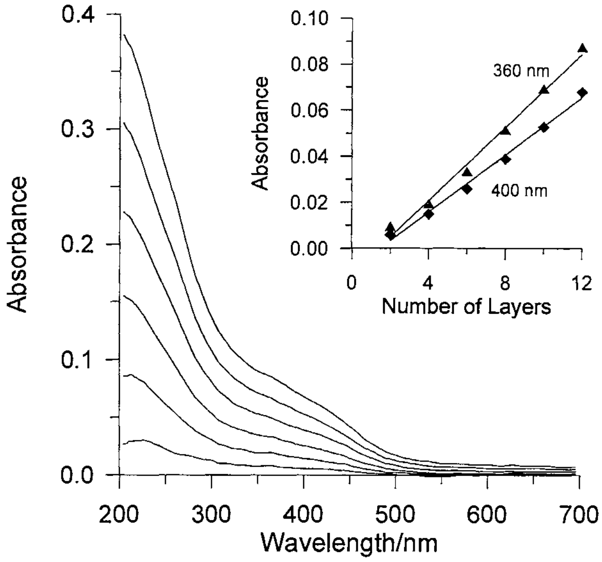


Figure 1. UV-Vis absorption spectra of alternating film deposition of PVP/CdS with different numbers of layers on a quartz slide. From the lower to the upper curves, the numbers of CdS layers is 2, 4, 6, 8.10 and 12. Inset: the relationship of absorbance at 360 and 400 nm vs the number of CdS layers.

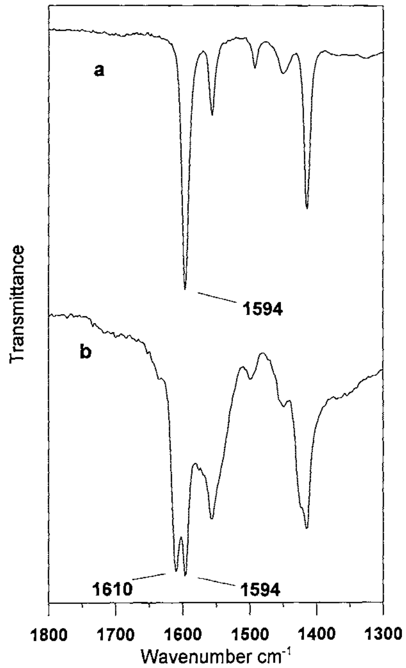


Figure 2. IR spectrum of (a) pure PVP and (b) PVP/CdS mulitlayers.

above steps.

UV-Vis spectra, obtained using a Shimadru 3100 UV-Vis-near-IR recording spectrophotometer, were used to monitor the self-assembly process of repeating the CdS and PVP layers. The CdS-DMF solution had a steep absorption onset at about 480 nm, which is blue-shifted relative to that of bulk CdS (520 nm). Figure 1 shows the UV-Vis absorption spectra of the multilayer film of CdS/PVP with different number of layers on a quartz slide. The similarity of the absorption spectra of the alternating films to that of the CdS-DMF solution implies that the CdS nanoparticles were assembled in the multilayer films successfully. The observed good linearity in the plots of absorbances vs the number of layers (inset of Figure 1) indicated a stepwise and uniform assembling process.

The driving force for the building up the CdS/PVP multilayer film was identified by infrared spectroscopy. Figure 2 shows the IR spectra of (a) pure PVP and (b) CdS/PVP multilayer film. By comparing curves a and b, it was noticed that a new peak at 1610 cm^{-1} appeared in the spectrum of the CdS/PVP multilayer film. Since the coordinate complexation between pyridine groups and metal ions usually exhibits this band due to the formation of coordination bonds,[6,9] we therefore considered that CdS nanoparticles was assembled into multilayer film based on the formation of coordinative bonds between the surface Cd atoms of CdS nanoparticles and the pyridine groups of the PVP. We also found colloidal CdS solution prepared by adding excess H_2S was unstable and didn't ensure the multilayer assembly. This means that CdS particles with a general S-rich surface do not have specific interaction with pyridine groups.

Preliminary studies indicate that a very similar strategy can be employed for the assembling nano-sized particles (such as, ZnS, ZnSe, ZnS:Mn) into thin films, and thus it should refer the reported method as an alternative way for the construction of nanoparticle and polymer hertero-structured thin film.

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