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Polyelectrolyte−Quantum Dot Multilayer Films Fabricated by Combined Layer-by-Layer Assembly and Langmuir−Schaefer Deposition

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Stable multilayer thin films, assembled by a combination of layer-by-layer processing of polyelectrolytes and inorganic quantum dot monolayers prepared using the Langmuir−Schaefer deposition procedure, have been examined. Film formation and structure are confirmed using UV−vis absorption measurements and fluorescence spectroscopy. Growth is shown to be linear over several polyelectrolyte−quantum dot multilayers. Films consist of either (trioctylphosphine/trioctylphosphine oxide)-capped CdSe (4.1 nm ± 0.16 nm) or dodecanethiol-capped Au quantum dots (6.0 nm ± 0.9 nm) within polyelectrolyte bilayers of the well-studied (poly(allylamine hydrochloride)/poly(styrene sulfonate)) system. Electrostatic and hydrophobic interactions combine as the basis for assembly using this versatile new procedure.

The introduction of layer-by-layer (LbL) assembly of polyelectrolytes from aqueous solution in the early 1990s enabled the formation of useful thin film architectures.[1−3] Subsequently, a variety of schemes for the formation of multilayer films were introduced, incorporating semiconductor or metal quantum dots (QDs), which utilized charged surface-passivating ligands on the QDs to facilitate aqueous LbL assembly.[4−8] While the advantages of LbL assembly, such as assembly from aqueous solution, and lack of a substrate shape constraint, are important when applied to mixed systems of polyelectrolytes and QDs, questions remain about the internal structure of the layers and the impact this internal structure may play in certain applications. Deposition of QDs directly from solution affords little control over many of the assembly parameters, such as the packing density of the QDs, and the amount of phase segregation between the QDs and the polyelectrolyte layers. The LbL assembly of polyelectrolytes produces films with highly interpenetrated layers.[9−12] This characteristic mixing of layers in an LbL film has been shown to translate closely to QD layers produced using the LbL approach.[5] In contrast, studies incorporating α-zirconium phosphate sheets[13] or clay sheets[14] in an LbL scheme present examples of preformed inorganic layers limiting the amount of interpenetration. In applications such as the production of organic light-emitting diodes (OLEDs), the precise deposition and controlled environment around the active layers (i.e., the QD layers) are of utmost importance. It has recently been shown that the amount of phase segregation and monolayer character of QD layers in QD−small molecule organic devices represents a major factor in device performance.[15]

Formation of Langmuir films is a viable route to the formation of QD monolayers, given they are capped with hydrophobic ligands. These films are typically studied after their transfer to solid substrates using the Langmuir−Blodgett (LB) technique.[16,17] Initial studies relied on traditional amphiphiles to form a monolayer on the subphase surface, either directly as capping groups stabilizing the QDs or onto which a layer of QDs could be synthesized or deposited. It was subsequently reported that as-synthesized trioctylphosphine/trioctylphosphine oxide (TOP/TOPO)-capped CdSe monolayers could be assembled on solid substrates using LB deposition.[18] Recently, LB-deposited Au nanoparticles have been incorporated into a metal−insulator−semiconductor (MIS) structure.[19] The related, more facile Langmuir−Schaefer (LS) deposition technique was used to form QD films from the same as-synthesized CdSe systems, although the LB dipping technique showed similar film transfer results.[20] The LS procedure consists of the horizontal lifting or

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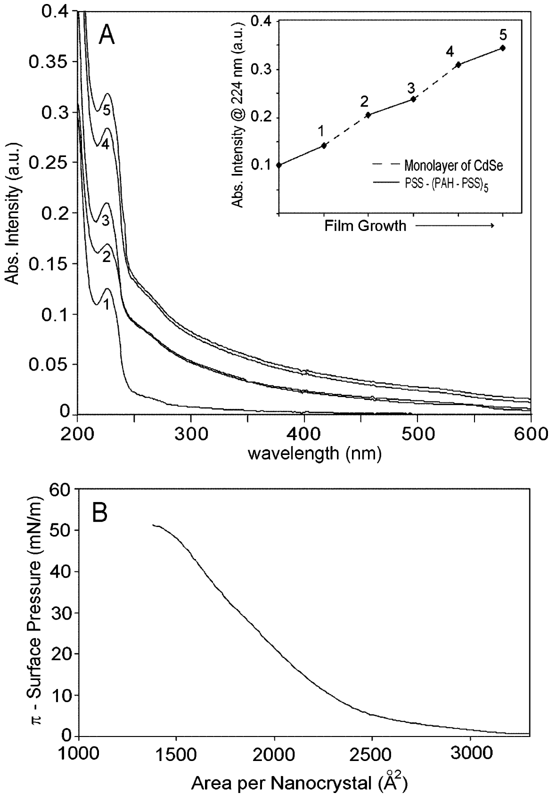

Figure 1. (A) UV−vis absorption characteristics of a multilayer film containing PSS−(PAH/PSS)$_5$ (spectrum 1) spaced by layers of CdSe QDs (spectrum 2). This process is repeated to produce the subsequent spectra. The inset shows a linear increase in the absorption maxima at 224 nm due to the polyelectrolyte layers (solid line) and the QD layers (dashed line). (B) Surface pressure versus area isotherm of CdSe QDs on a water subphase.

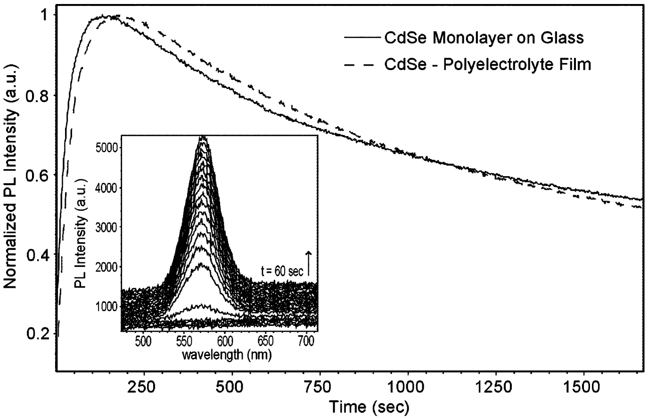

Figure 2. Normalized photoactivation kinetics for a CdSe QD solid deposited directly on glass (solid line) and a CdSe−polyelectrolyte film (dashed line). The inset presents the photoluminescence spectrum of the CdSe−polyelectrolyte film during the initial 60 s of the photoactivation process.

stamping of the Langmuir film onto a solid substrate held parallel below or above the QD film surface. In this letter, we highlight our effort to combine the established LbL route for polyelectrolyte film formation with the LS deposition of semiconductor and metal QDs to fabricate well-ordered multilayer films.

The LbL process for the formation of polyelectrolyte films fabricated on glass or quartz coverglass containing a priming layer of poly(ethylene imine) (PEI), poly(allylamine hydrochloride) (PAH), and poly(styrene sulfonate) (PSS) has been described elsewhere.[21] PAH and PSS were purchased from Aldrich Inc., and PEI was purchased from Polysciences Inc. All polyelectrolyte materials were used without further purification. The TOP/TOPO-capped CdSe QDs (mean size, 4.1 nm ± 0.16 nm) were prepared using a slight variation on the lyothermal synthesis developed by Bawendi and coworkers.[22,23] Dodecanethiol-capped Au QDs (mean size, 6.0 nm ± 0.9 nm) were synthesized using the standard protocol in aqueous media by reduction of auric acid in the presence of sodium citrate and tannic acid.[24] The CdSe or Au QDs are deposited from hexanes at the air−water interface using a Langmuir film balance (NIMA 611, Coventry, U.K.). The film is transferred to a solid substrate using the Schaefer method at a surface pressure of 30−35 mN/m. Previous work has shown this transfer process results in a close-packed glass with ordered domains of QDs on the order of 100 nm.[20]

The fabrication of multilayer films is monitored by UV−vis spectroscopy. Figure 1 presents absorption data for a multilayer film containing layers of TOP/TOPO-capped CdSe QDs deposited between $5^{1}/_{2}$-bilayer sections of PSS/PAH LbL film. The deposition begins with deposition of the priming PEI layer on a quartz substrate. Next, a $5^{1}/_{2}$-bilayer film of PSS−(PAH/PSS)$_5$ is deposited. The absorption of this $5^{1}/_{2}$-bilayer film is shown in Figure 1a (spectrum 1), with the absorption of the phenyl group of PSS the only major feature centered at 224 nm. A layer of CdSe QDs is then deposited on the polyelectrolyte surface, as shown in Figure 1a (spectrum 2), resulting in the addition of the absorption spectrum of 4.1 nm CdSe in the range 200−550 nm. The inset in Figure 1a plots the two-stage linear increase in the absorption intensity owing to both the polyelectrolyte bilayers and the CdSe within the multilayer film. It is important to note that there is little deviation from a linear growth regime for both the QD and the LbL layers (shown by a near-constant slope in both growth regions), showing that no loss of QD material is seen during the immersion into subsequent LbL solutions. This is shown clearly when the QD absorption is unchanged while the LbL layers are deposited, while the absorption attributed to the PSS layers increases (Figure 1a, spectrum 3). In addition, the absorption values are constant within experimental error across a given sample, suggesting a uniform film coating at each deposition step. Figure 1b shows a typical pressure−area isotherm for CdSe QDs compressed atop a water subphase. No substantial change is seen in the isotherm upon expansion and recompression.

The inclusion of CdSe monolayers within an LbL framework is also confirmed by photoluminescence studies done on the completed multilayer film. Previous work from our laboratory has demonstrated that CdSe monolayer films on glass exhibit a photoactivation process when illuminated under ambient conditions.[20] This phenomenon has subsequently been utilized for applications in patterning[25] and data storage[26] in QD films. The photoactivation kinetics is heavily dependent on many factors including the monolayer characteristic of the QD film. Figure 2 presents photoluminescence data from the

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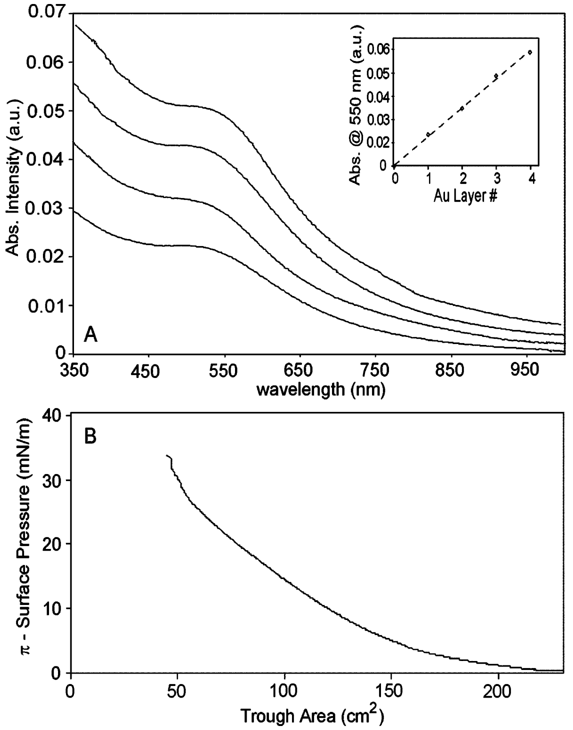

Figure 3. (A) UV−vis absorption spectra of a film containing layers of Au QDs spaced by polyelectrolyte layers with the structure PSS−(PAH/PSS)$_5$. The inset shows the linear increase of the absorption maximum of the plasmon band of the Au QDs at 550 nm. (B) Surface pressure versus area isotherm of Au QDs on a water subphase.

photoactivation of a QD−polyelectrolyte film, as well as a comparison between the kinetics of the photoactivation for a QD−polyelectrolyte film and a CdSe monolayer on a glass substrate. The agreement between the photoactivation kinetic traces for the monolayer of CdSe on glass and that within an LbL film confirms the transfer of a stable monolayer onto a polyelectrolyte surface, as well as the stability of that monolayer to further LbL processing.

Another significant advantage of utilizing the combination of LbL and LS for the fabrication of multilayer films is its ease of application to any QD system possessing capping ligands that form a complete hydrophobic layer suitable for deposition on a water subphase. To illustrate this point, the same process undertaken to form CdSe layers within an LbL framework was commenced with dodecanethiol-capped Au QDs. Figure 3a presents absorption measurements for a multilayer film containing layers of dodecanethiol-capped Au QDs deposited between $5^1/_2$-bilayer films with the structure PSS−(PAH/PSS)$_5$. The deposition and layer growth of the Au QD layers was confirmed using visible absorption resulting from the plasmon band absorption of the Au QDs with a bandedge at 550 nm. Figure 3b shows a typical pressure−area isotherm for Au QDs compressed atop a water subphase.

Similar growth regimes are observed whether the Au QDs (or CdSe QDs) are deposited atop a PAH or PSS surface layer, highlighting the point that substrate surface charge is not the sole driving force for assembly in this preformed QD solid−polyelectrolyte system. It has been shown that alternative driving forces, in this case hydrophobic interactions[27−31] between the QD capping ligands and the polyelectrolyte backbone, help facilitate assembly and film stability. In particular, these hydrophobic interactions may be accentuated given the polyelectrolyte film is dried in an ambient environment before deposition of the QD monolayers.[32]

The combination of the LbL assembly of polyelectrolytes with Langmuir−Schaefer deposition of controlled monolayers of QDs presents a novel route for the formation of multifunctional thin film materials. By utilizing as-synthesized QDs capped with organic capping ligands, this procedure eliminates ligand-exchange reactions needed to integrate charged ligands into a purely LbL procedure. The hydrophobic interaction between the capping ligands and the polyelectrolyte backbone that drives assembly allows any QD material to be utilized. The Langmuir−Schaefer deposition process allows specific control of the packing density of QDs within a given layer, by depositing at different points in the pressure−area isotherm, onto the polyelectrolyte surface. We are continuing high-resolution microscopy and X-ray diffraction studies to precisely determine the QD layer packing control as well as examining the electroluminescence properties of this thin film system. We are also investigating other QD−polyelectrolyte film structures.

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