

무극성 용매에서의 나노입자 Layer-by-Layer Assembly

Non-Polar Media Layer-by-Layer Assembly of Nanomaterials

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1. Introduction

Nanostructured thin films, composed of multiple materials such as nanoparticles and polymers, possess distinctive combinations of properties that make them useful for advanced applications. Electrodes in various energy conversion and storage devices, for example, are nanostructured thin films that possess desirable transport, catalytic and electrical properties. Needless to say, the structure of these nanostructured electrodes will significantly influence the performance and efficiency of the devices. As simple as it may sound, however, the fabrication of nanostructured thin films with precisely controlled structure and composition using a simple scalable method presents a major challenge.

Layer-by-layer (LbL) assembly involves sequential deposition of oppositely charged species onto surfaces (Figure 1), and presents a simple yet versatile solution-based method to generate nanostructured thin films. Because molecularly thin layers of materials are sequentially deposited at a time, this method provides an enormous level of control over the structure and composition of the resulting thin films. Many examples of functional thin films have been reported based on this method, making it one of the most promising “bottom-up” approaches for fabricating nanostructured thin films for advanced applications.

The LbL assembly, to date, has mostly been limited to the fabrication of thin films using materials dissolved in aqueous solutions. This conventional practice places a major obstacle to generating functional nanostructured thin films because a large number of useful and unique nanoparticles and polymers are synthesized and stable in non-aqueous non-polar solvents only. These materials include semiconducting, catalytic and magnetic nanoparticles, as well as conducting polymers. In their native states, these materials are not suitable candidates for LbL assembly because they do not acquire charge and, thus, are not stable in water. Enabling LbL assembly of water-insoluble nanomaterials directly in non-polar media would be transformative because functional thin films can be generated without the extra processing steps of ligand exchange to make these materials water-soluble and ionizable, and without the possible loss of the functionality of nanomaterials due to surface treatments. This highlight will review some of recent developments in layer-by-layer assembly of nanomaterials in non-polar media.

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2. Charge-Inducing Agent Mediated Layer-by-Layer Assembly in Non-Polar Media

LbL assembly in non-polar solvents (especially when permittivity (ϵ) is below 5) is fundamentally challenging because materials dispersed in such solvents generally do not become charged. Thus, a nanomaterial cannot interact with another nanoparticle *via* electrostatic interactions to form nanoassemblies such as films. This fundamental limitation has significantly inhibited attempts to perform LbL assembly in non-polar media despite the fact that a lot of nanoparticles and polymers with unique properties are only soluble in these solvents. The reason behind the difficulty associated with charging particles in apolar solvents can be explained by estimating the Bjerrum length.¹ The Bjerrum length ($\lambda_B = e^2 / 4\pi\epsilon_0\epsilon k_B T$) represents a characteristic separation distance between two oppositely charged monovalent ions at which the thermal energy ($k_B T$) becomes similar to the electrostatic energy between the ions. λ_B is only 0.7 nm in water ($\epsilon \sim 80$) at room temperature, whereas it is 28 nm in hexadecane ($\epsilon \sim 2.0$). This simple calculation shows that for simple electrolytes to dissociate completely, a thick (14 nm) solvation layer has to form spontaneously. Thus, it is energetically unfavorable to form charged species in apolar solvents.

Although materials dissolved in apolar solvents are unlikely to become charged, reports have demonstrated that particles in non-polar solvents can become charged when a charge inducing agent (CIA), typically an amphiphilic molecule, is added to non-polar solvents.^{2,4} Colloidal particles in non-polar media become stable through electrostatic repulsion,^{2,3} and repulsion between particles has been measured using optical methods.⁵ These results indicate that electrostatic interactions in non-polar solvents are long-ranged (100s' nm – 10s' μ m) and their interactions can be significant under appropriate

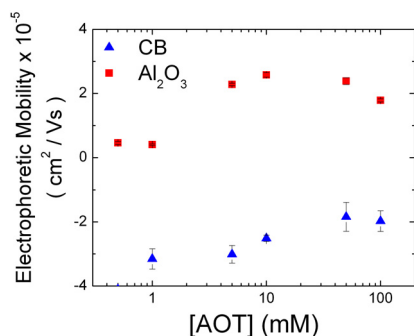


Figure 1. Electrophoretic mobility of Al_2O_3 and CB nanoparticles in AOT/toluene mixture.

conditions. The presence of CIA micelles and the disproportionation of CIA micelles resulting in the generation of charged micelles are believed to play an important role in imparting surface charge to particles.⁶

Taking advantage of the charge-inducing properties of a charge inducing agent (CIA), we have successfully fabricated conductive nanostructured thin films by LbL assembly of Al_2O_3 and carbon black (CB) nanoparticles in toluene.⁷ Interestingly, when CB and Al_2O_3 nanoparticles are dispersed in sodium di-ethylhexylsulfosuccinate (also known as, Aerosol-OT (AOT)) doped toluene, CB became negatively charged, whereas Al_2O_3 nanoparticles acquired positive charge as determined using electrophoretic mobility analysis (Figure 1). The electrophoretic mobility of each nanoparticle also depended on the concentration of AOT. The difference in the charging behavior of these two particles in non-polar media is believed to be due to the difference in the acidity of nanoparticle surface; however, the exact physicochemical nature of surface charge is not clearly known and warrant future investigation.^{1,6,8}

The sequential deposition of the two oppositely charged Al_2O_3 and CB nanoparticles on glass surfaces exhibits a number of hallmarks of LbL assembly. The growth behavior of LbL-assembled films, quantified by UV-Vis absorbance (Figure 2), was linear. In contrast, when a substrate was repeatedly exposed to a CB solution without alternating Al_2O_3 deposition, little film growth was observed (control in Figure 2a), suggesting that non-specific adsorption of CB is a film growth mechanism. The film growth also depended on the concentration of AOT in each nanoparticle suspension (Figure 2b). Such dependence is similar to controlling the structure and properties of aqueous LbL

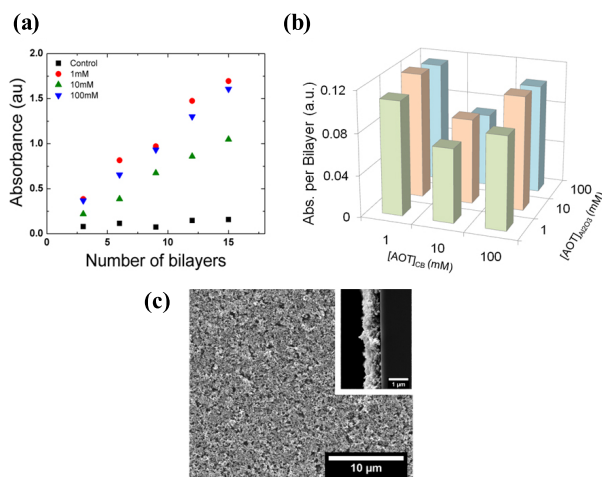


Figure 2. (a) UV-Vis spectra of Al_2O_3 /CB LbL films, (b) average absorbance per bilayer as a function of AOT concentration in nanoparticle suspensions, (c) SEM image of a CB/alumina LbL film, Inset shows a cross-sectional SEM image.

films by varying the pH and ionic strength of nanoparticle/polymer solutions.⁹⁻¹² Scanning electron microscopy (SEM) of CB/Al₂O₃ films (Figure 2c) showed the high uniformity of the LbL film over a large area. The CB/Al₂O₃ LbL films are also conductive because of the percolation of CB nanoparticles in the nanocomposite structure. Most importantly, the conductivity of the CB/Al₂O₃ LbL films could be tuned by simply changing the concentration of AOT (Table 1).

We have further extended this approach to generate photocatalytic and conductive nanocomposite thin films composed of multi-walled carbon nanotube (MWCNT) and TiO₂ nanoparticles.¹³ Previously, MWCNT have been typically incorporated into LbL films by oxidizing them to increase their water solubility.¹⁴ However, the oxidation of MWCNT can drastically change their pristine structure, which in turn adversely impact their unique electrical and mechanical properties.^{15,16} Such treatment is especially undesirable for many applications involving energy storage and conversion devices such as dye-sensitized solar cells¹⁷ and PEM fuel cells.¹⁸ The newly developed non-polar media-based LbL method circumvents the typical requirement of water solubility of MWCNT.¹⁴ The photocatalytic activity of TiO₂/MWCNT nanocomposite thin film, fabricated based on our new approach, showed a marked improvement over that of pure TiO₂ films likely due to the incorporation of pristine MWCNT and the suppression of electron-hole recombination (Figure 3) upon photoactivation.¹⁹

Table 1. Summarizes the Conductivity Measurements of CB/Alumina Films Assembled at Different AOT Concentrations, Reproduced with Permission from American Chemical Society⁷

AOT Concentration (mM)	Conductivity (S/m)
1	28.5±0.4
10	8.54±0.01
100	21.31±0.02

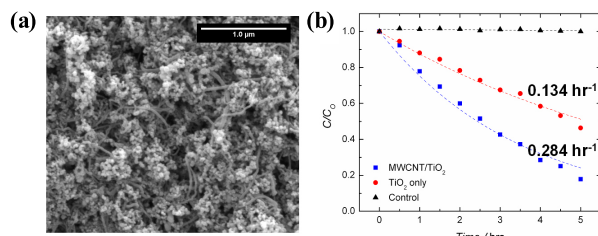


Figure 3. (a) SEM image of MWCNT/TiO₂ nanocomposite thin film generated using LbL assembly in non-polar media. (b) Photocatalytic activity of MWCNT/TiO₂ (filled blue square) compared to TiO₂ film (filled red circle). Photocatalytic activity of each film was tested by monitoring the degradation of an organic dye under UV irradiation (365 nm). Reproduced with permission from American Chemical Society.¹³

3. Layer-by-Layer Assembly in Organic Media using Nucleophilic Substitution

Another important breakthrough that enables layer-by-layer assembly of nanoparticles in non-polar solvent relies on using a nucleophilic substitution reaction.^{20,21} Cho *et al.* have shown that alternating layers of highly hydrophobic CdSe@ZnS quantum dots (QDs) capped with 2-bromo-2-methylpropionic acid (BMPA) in apolar solvents such as toluene or hexane and poly (amidoamine) (PAMA) dendrimer in ethanol can be deposited based on a nucleophilic substitution reaction between Br and NH₂ (Figure 4). This approach allowed for the formation of LbL films with a high packing density of nanoparticles, up to 58% due to the absence of electrostatic repulsion between nanoparticles. The incorporation of highly hydrophobic QD nanoparticles also led to the fabrication of photoluminescent films with high stability in air and humid conditions. This study was further extended to

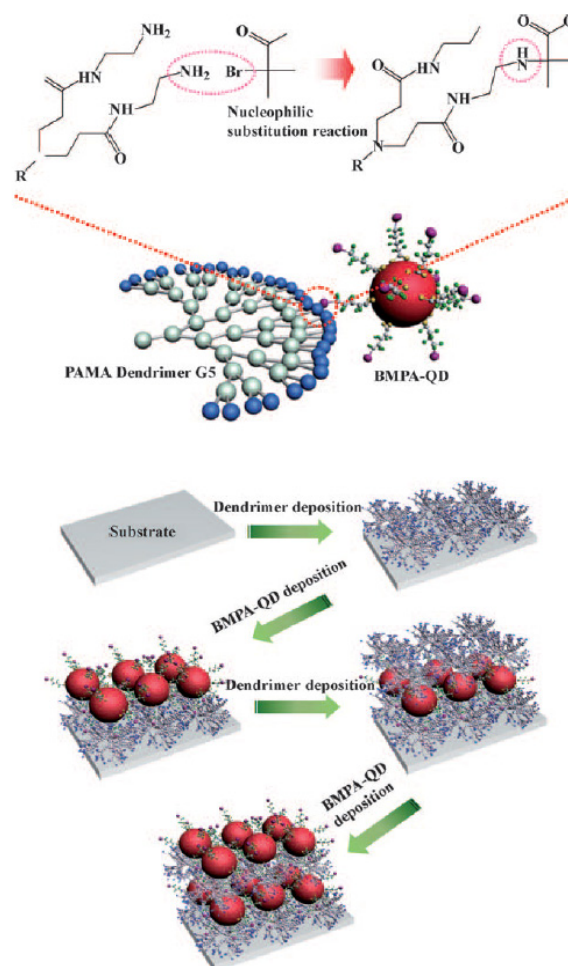


Figure 4. Schematic illustration of apolar layer-by-layer assembly based on nucleophilic substitution reactions between amino and bromo group.¹⁹ Reproduced with permission from Wiley.

successful preparation of multifunctional silica colloids by layer-by-layer deposition of 2-bromo-2-methylpropionic acid (BMPA)-stabilized quantum dots (BMPA-QDs) and BMPA-stabilized iron oxide particles (BMPA-Fe₃O₄), along with amine-functionalized poly (amidoamine) (PAMA) dendrimers in organic media. Oleic acid stabilizers used in the synthesis of nanoparticles in non-polar solvents were exchanged with BMPA and subsequently incorporated into LbL coatings on silica colloids using the nucleophilic substitution reaction. The multifunctional colloids densely coated with nanoparticles showed excellent superparamagnetism, photoluminescence, and magneto-optical tuning properties with long-term stability in nonpolar solvents.

4. Summary and Outlook

In summary, recent development clearly demonstrates that layer-by-layer assembly can be extended to generate nanostructure thin films made of multiple functional nanomaterials in non-polar solvents. In one approach, a charge inducing agent, AOT, was used to impart opposite charges onto metal oxide nanoparticles and carbon nanomaterials, respectively. We showed that LbL assembly of CB/alumina as well as TiO₂/MWCNT nanocomposite films is enabled by the addition of AOT as a charge inducing agent and that the concentration of AOT is a critical processing condition that controls the structure and properties of the nanocomposite films. In another approach, nucleophilic substitution reaction between amine- and bromo-groups enabled the fabrication of functional LbL films on a variety of substrates. These simple methods of using a charge inducing agent such as AOT or of using the nucleophilic substitution reaction to enable layer-by-layer assembly in non-polar media will significantly enhance the versatility of LbL assembly as a universal film fabrication method.²¹⁻²⁴

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